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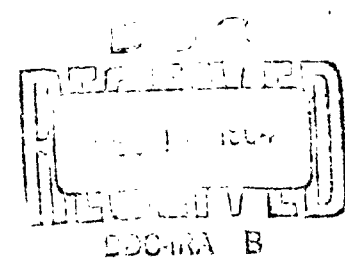
95 pages
+ App. I and App. II

FINAL TECHNICAL SUMMARY REPORT

INVESTIGATE THE PROPERTIES OF GLASSES TRANSMITTING

IN THE 3 to 5 and 8 to 14 MICRON WINDOWS

OFFICE OF NAVAL RESEARCH CONTRACT NO. Nonr-4212(00)

In Cooperation with

Advanced Research Projects Agency

Department of Defense

Order No. ARPA269

Period Covered: 1 June 1963 to 31 August 1964

SCA 43,600

FINAL TECHNICAL SUMMARY REPORT
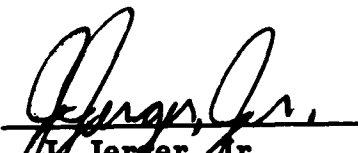
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ABSTRACT

This program was carried out in two parts, and the final report is divided accordingly.

Part I consisted of measurements of the properties of 20 glasses selected from the Servo proprietary composition field As-S-Se-Te. The primary selection criteria were softening temperature in excess of 100°C, good transmittance in the 2 to 5 and/or 8 to 14 micron atmospheric windows, and the widest possible range of index of refraction and dispersion characteristics.

Part I includes the measurement of optical, chemical, thermal, physical and electrical properties of the 20 selected glasses.

The procedures and equipment used for property measurements are detailed in Appendix I and are essentially the same as those used in a previous investigation under ARPA-ONR Contract No. Nonr 3647 (00) which was limited to glasses having good transmission from 8 to 14 μ. Some modifications in test methods were made to increase the validity and reliability of the data.

A mathematical evaluation of the reliability of the measurements data is presented and discussed in Appendix II.

Tables of the more pertinent properties arranged in descending order are included so that selection of material by the designer may be facilitated.

Part II included a study of the long wavelength absorption characteristics of As-Se-Te glasses and the effects of composition, formulation procedure and impurities on the absorption of these glasses. In addition, an investigation of the effects of combined high pressures and temperatures on the density, refractive index and IR transmission of representative compositions was carried out with the objective of achieving an improved understanding of the fundamental structure of chalcogenide glasses.

An absorption band common to most of these glasses which is centered at about 12.8 microns has been related to oxide impurity content, probably As_2O_3, and processing techniques were demonstrated which would eliminate or substantially reduce this band. This phenomenon can be extrapolated to other glasses based on the same glass-forming elements.

High pressure-temperature studies indicate a degree of residual compaction in the glasses which tends to confirm the concept of basic structure as having the form of cross-linked chains or laminae which is commensurate with three-fold coordination. The addition of appreciable percentages of germanium seems to indicate a change from three-fold to four-fold coordination.

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I - INTRODUCTION

1. The advancing state-of-the-art of infrared technology as applied to sensors for operational military and space systems has resulted in a pressing need for optical systems having resolution capabilities and fields of view considerably better than those heretofore available.

To meet this need, multi-element refractive systems are required. Reflective and catadioptric systems present problems of self-masking, stray radiation, off-axis aberrations and spatial volume requirements which frequently render them impractical. Refractive systems allow greater compactness and in-line, unobscured operation in addition to their potential for high resolution and wide angular fields of view. The designer of infrared optical systems, however, is severely handicapped by the limited selection of optical materials from which he can choose for the correction of both spherical and chromatic aberrations. Only a few useful materials which are optically compatible in index and dispersion are available for infrared systems design as compared with scores of glasses useful for visible optical systems.

In addition, chromatic corrections for the IR must be effected over wavelength ranges which are an order of magnitude greater than those of visible light.

2. Several years ago at Servo Corporation of America, an extensive series
    of glass compositions containing two or more of the elements As-S-Se-Te
    was discovered. These glasses transmitted infrared radiation - some to
    16 μ and beyond. Although their physical and thermal properties were
    less than optimum compared to silicate glasses, the range of transmission,
    refractive index and dispersion characteristics was such that they were
    considered to be potentially useful for many applications of high performance
    refractive systems beyond the existing state-of-the-art in IR optical design.

    Accordingly, ARPA-ONR Contract No. Nonr 3647(00) was set up to select
    and measure the properties of glasses suitable for optical systems opera-
    ting in the 8 to 14 micron atmospheric window. Twenty different composi-
    tions were selected and their properties determined.

    During the course of the above program, it was discovered that as little
    as 5% by wt. sulfur in a glass would limit its transmission to a maximum
    wavelength of about 13.5μ. The investigation was limited, therefore, to
    glasses in the As-Se-Te system, and a large number of glasses useful in
    the shorter wavelengths were eliminated from consideration.

3. Chromatic aberrations are considerably more difficult to correct in the
    short wavelengths because of the greater short wavelength slope of the
    dispersion curves of all optical materials.

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Because of this, the realization that the problems inherent in the design of optical systems for the 2 to 5 μ atmospheric window were even more severe than in the longer wavelengths, led to the initiation of Part I of the present program for the selection and evaluation of glasses not considered in the previous investigation.

The properties were measured of twenty additional compositions which were selected according to the criteria:

a) Good transmission in the 2 to 5 and/or 8 to 14 μ atmospheric windows.

b) Softening temperature above 100°C.

c) Maximum range of index and dispersion characteristics.

4. Various factors, including composition, impurity concentration, thermal history and melting procedure can affect the long wavelength absorption characteristics of chalcogenide glasses.

In the evaluation of glasses containing As, Se and Te, a particularly well-defined absorption band centered at about 12.8 μ was noted in most of the compositions measured. Some preliminary experimentation indicated that this band could be markedly reduced by control of the thermal history of the glasses, i.e., "quenching" the glasses from above the liquidus temperature to a temperature well within the annealing range. The possibility was considered that this absorption was caused by the precipitation of a sub-crystalling phase distributed uniformly throughout

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the melt during slow cooling. Other possible causes such as those listed above were also considered.

In any case, it was felt that a study of the variations of long wavelength absorption in these glasses as a function of formulation and processing parameters would provide data significant to the understanding of the fundamental aspects of structural effects on infrared absorption.

Part II of this program, therefore, was established to investigate the interaction of long wavelength radiation with vitreous solids with respect to the internal structure of the materials as determined by the above factors.

II - PART I - PROPERTIES OF SELECTED IR TRANSMITTING GLASSES

1. ### General

    This section describes the selection of glasses for evaluation and presents measurement data obtained. For a detailed description of equipment and measurement procedures refer to Appendix I.

    The criteria for selection of glasses for complete property measurements were:

    a) Softening temperature greater than $100^{\circ}C$.

    b) Good transmission in the 2 to 5 and/or 8 to 14 micron atmospheric windows.

    c) Broadest possible range of refractive index and dispersion characteristics.

2. ### Selection of Glasses for Preliminary Investigation

    2.1 A system of evaluating glass melts was developed to determine the extent and quality of glass formation. This was used to classify 297 compositions of various combinations of arsenic, sulfur, selenium and tellurium. The method involved a microscopic examination of a cleaved section of a 50 gram sample. Three gradations of quality were established:

    a) Good glass

    b) Partially crystalline

    c) Devitrified on aging

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The 297 glasses were distributed in composition fields as follows:

Composition Field	Number of Glasses
As-S-Se	69
As-S-Te	58
As-S-Se-10%Te	49
As-S-Se-20%Te	46
As-S-Se-30%Te	43
As-S-Se-40%Te	32
Total	297

2.2 From this group of 297, the glasses that were partially crystalline or divitrified on aging were eliminated from further consideration. This narrowed the group down to 137 glasses distributed as follows:

Composition Field	Number of Glasses
As-S-Se	28
As-S-Te	19
As-S-Se-10%Te	35
As-S-Se-20%Te	25
As-S-Se-30%Te	17
As-S-Se-40%Te	13
Total	137

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2.3 Further examination was done to select glasses which softened above 100°C. A rapid test designated "pyramid softening temperature" determination was used for this purpose. It was originally developed under Nonr 3647(00) and is described in Appendix I. The above test narrowed the number of glasses down to 94. These were distributed in the composition field as follows:

Composition Field	Number of Glasses
As-S-Se	22
As-S-Te	18
As-S-Se-10%Te	22
As-S-Se-20%Te	16
As-S-Se-30%Te	9
As-S-Se-40%Te	7
Total	94

2.4 Transmission samples 20 mm diameter by 2 mm thick of the 94 glasses were ground and polished and transmittance measured from 2 to 16 microns. Those glasses exhibiting good transmittance were distributed as follows:

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Composition Field	Number of Glasses
As-S-Se	8
As-S-Te	5
As-S-Se-10%Te	7
As-S-Se-20%Te	9
As-S-Se-30%Te	6
As-S-Se-40%Te	5
Total	40

2.5   The index of refraction of these 40 glasses was measured at three wavelengths using the rapid refractometer (see Appendix I) in order to get a good approximation of the refractive properties. From these 40, the 20 glasses having the widest range of refractive index and dispersion characteristics were selected for complete property measurements. Their compositions in weight percent are shown in Table I.

3.   Properties Determined

The properties listed below were determined for each of the twenty glasses selected.

3.1   Optical Properties

a) Transmittance, 2 to 16 μ

b) Reflectance, 2 to 16 μ

c) Index of refraction, 2 to 16 μ

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3.2 Thermal Properties

a) Specific heat

b) Thermal Conductivity

c) Softening point

d) Critical point

e) Coefficient of Thermal expansion

f) Reworkability

3.3 Chemical Properties

3.3.1 Solubility (grams/exposed surface area)	Temp.
a) Water	25°C
b) Water	90°C
c) Ammonium Hydroxide, 0.3 N	60°C
d) Potassium Hydroxide, 0.4 N	60°C
e) Hydrochloric acid, 1.0 N	60°C
f) Nitric acid, 1.1 N	60°C
g) Sulfuric acid, 2.1 N	60°C
h) Ethyl Alcohol, 90% (vol.)	60°C

3.4 Electrical Properties

a) Resistivity

b) Dielectric Constant

3.5 Mechanical Properties

a) Specific Gravity

b) Compressive strength

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3. 5   Mechanical Properties (continued)

    c) Tensile strength

    d) Knoop hardness

    e) Young's Modulus

4.   Results

The results obtained are indicated as follows:

4. 1   Optical Properties

Infrared transmission, reflectance and refractive indices from 2 to 16 microns are shown in Figures 1 to 20.

4. 2   Thermal Properties

Thermal properties are shown in Table 2.   The twenty glasses are designated in descending order of softening point in Table 2A.

4. 3   Chemical Properties

Table 3 lists solubilities in each of the eight reagents.

4. 4   Electrical Properties

Dielectric constants (at one megacycle/sec.) and resistivities are listed in Table 4.

4. 5   Mechanical Properties

Mechanical properties are given in Table 5.

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FIGURE 1.

OPTICAL PROPERTIES OF GLASS NO. A-21

WAVELENGTH - MICRONS

FIGURE 2.

OPTICAL PROPERTIES OF GLASS NO. A-22
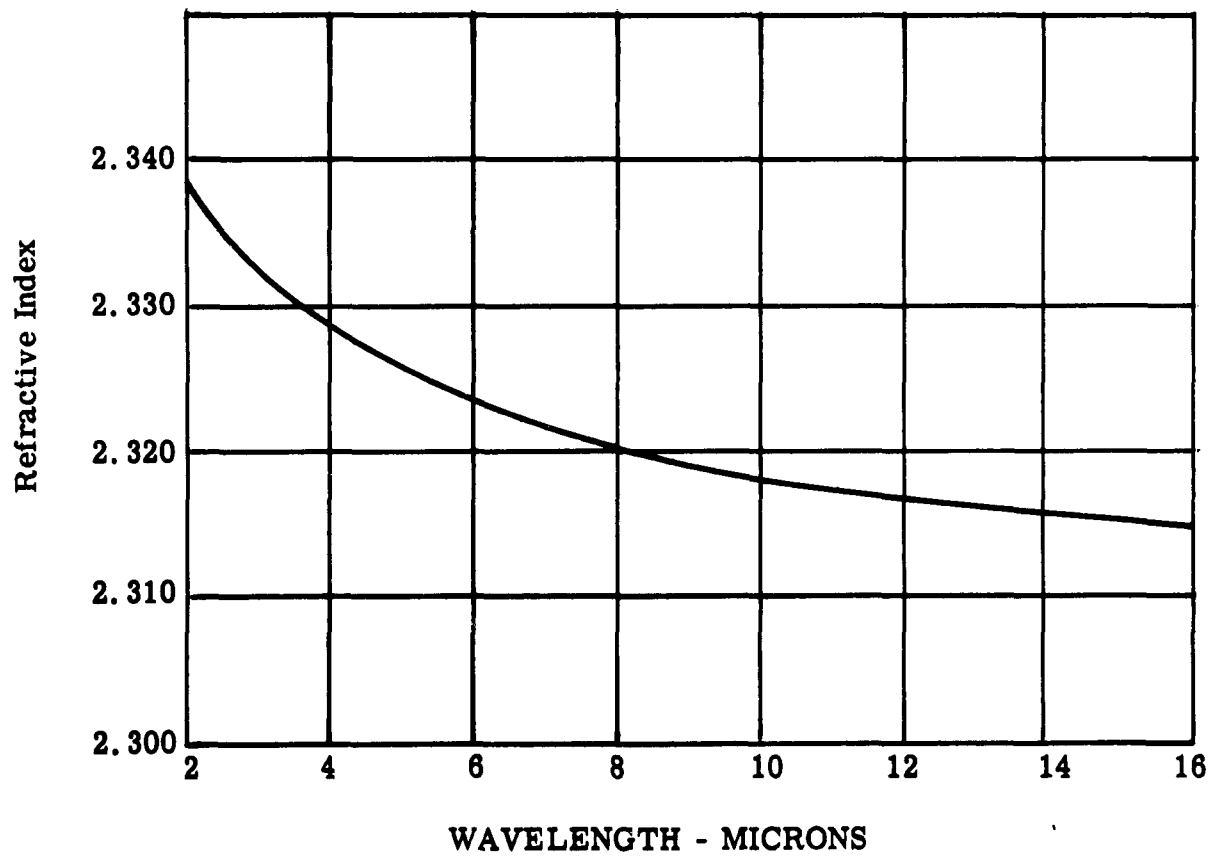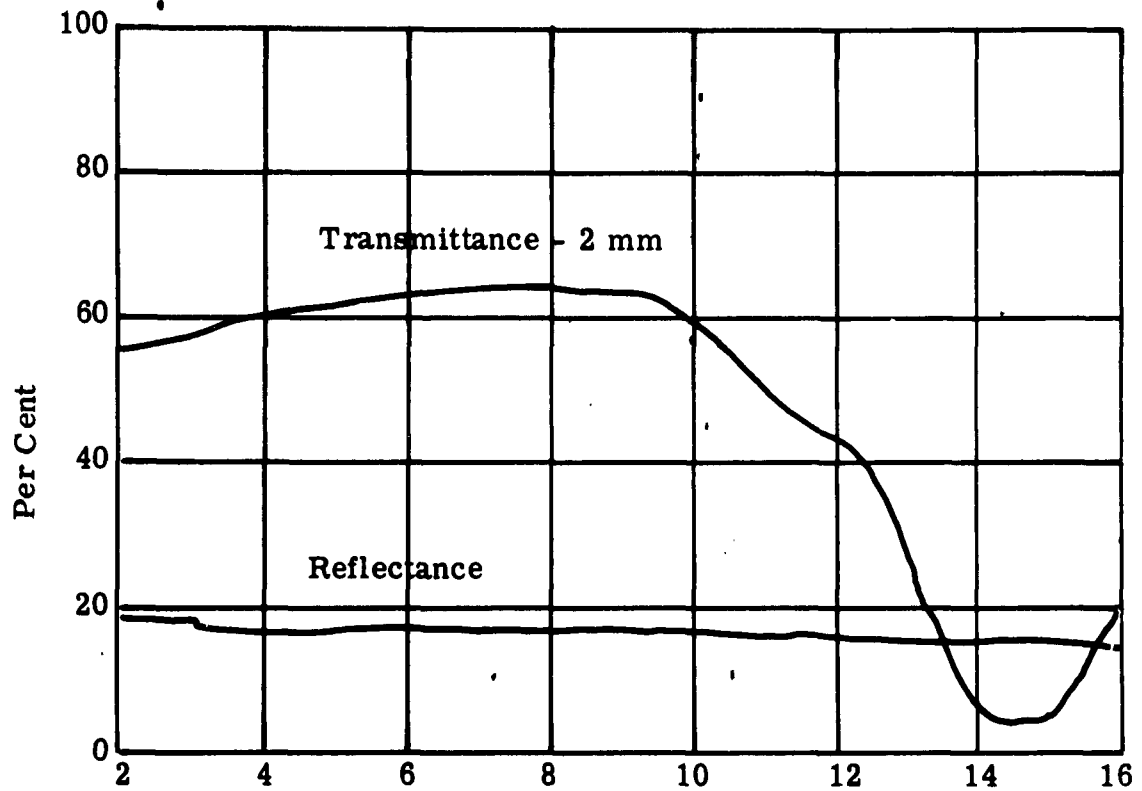
FIGURE 3.

OPTICAL PROPERTIES OF GLASS NO. A-145

WAVELENGTH - MICRONS
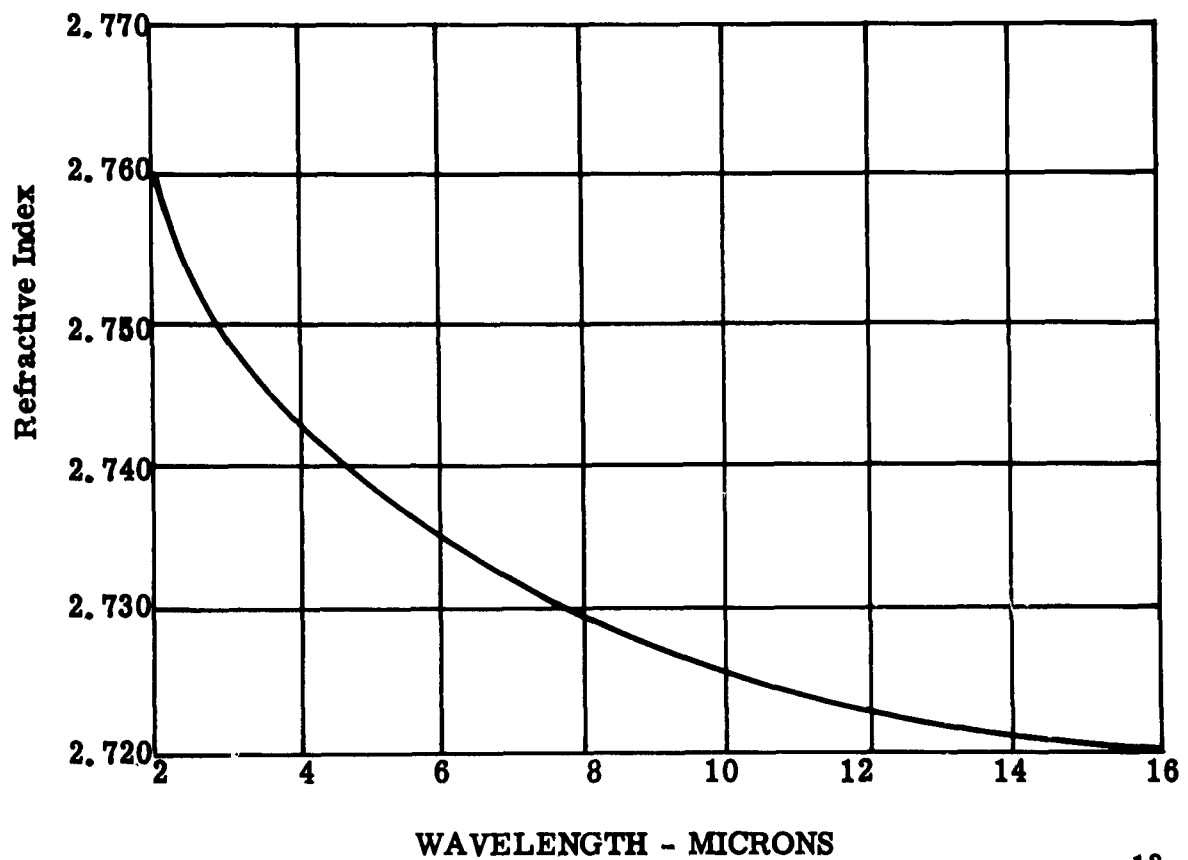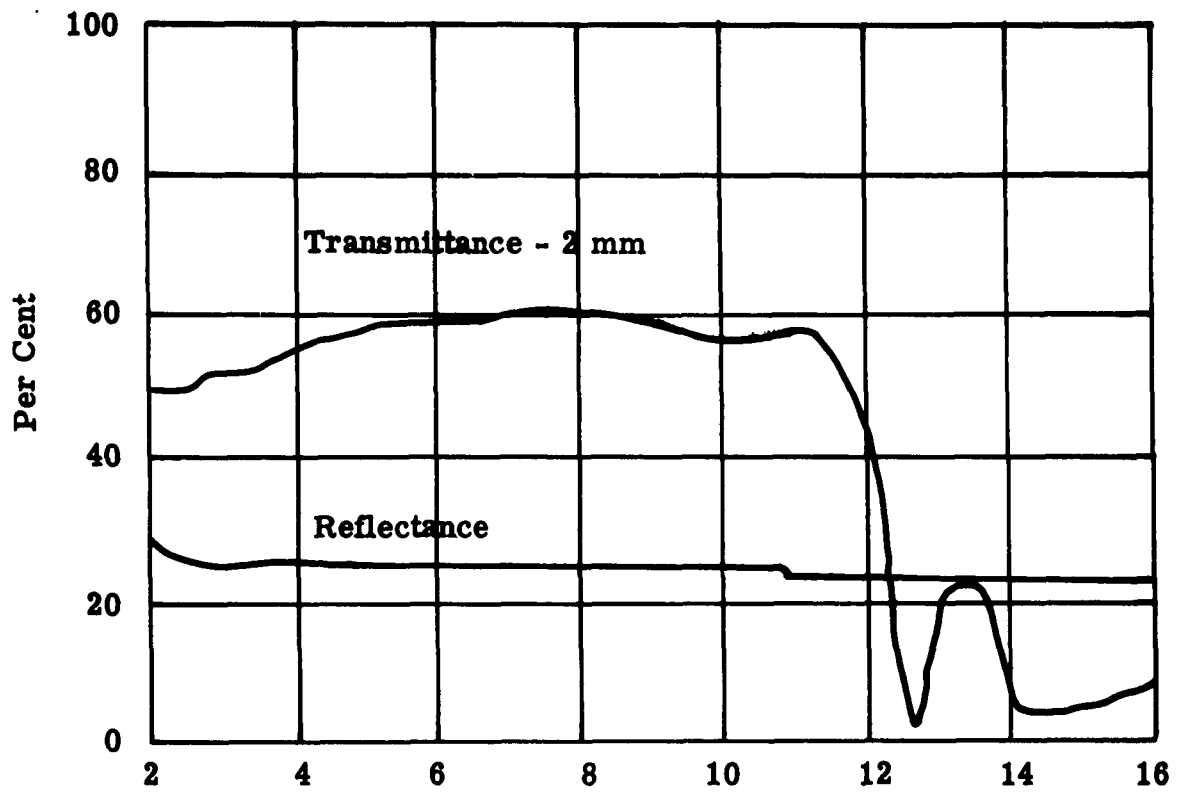
FIGURE 4.

OPTICAL PROPERTIES OF GLASS NO. A-160

WAVELENGTH - MICRONS
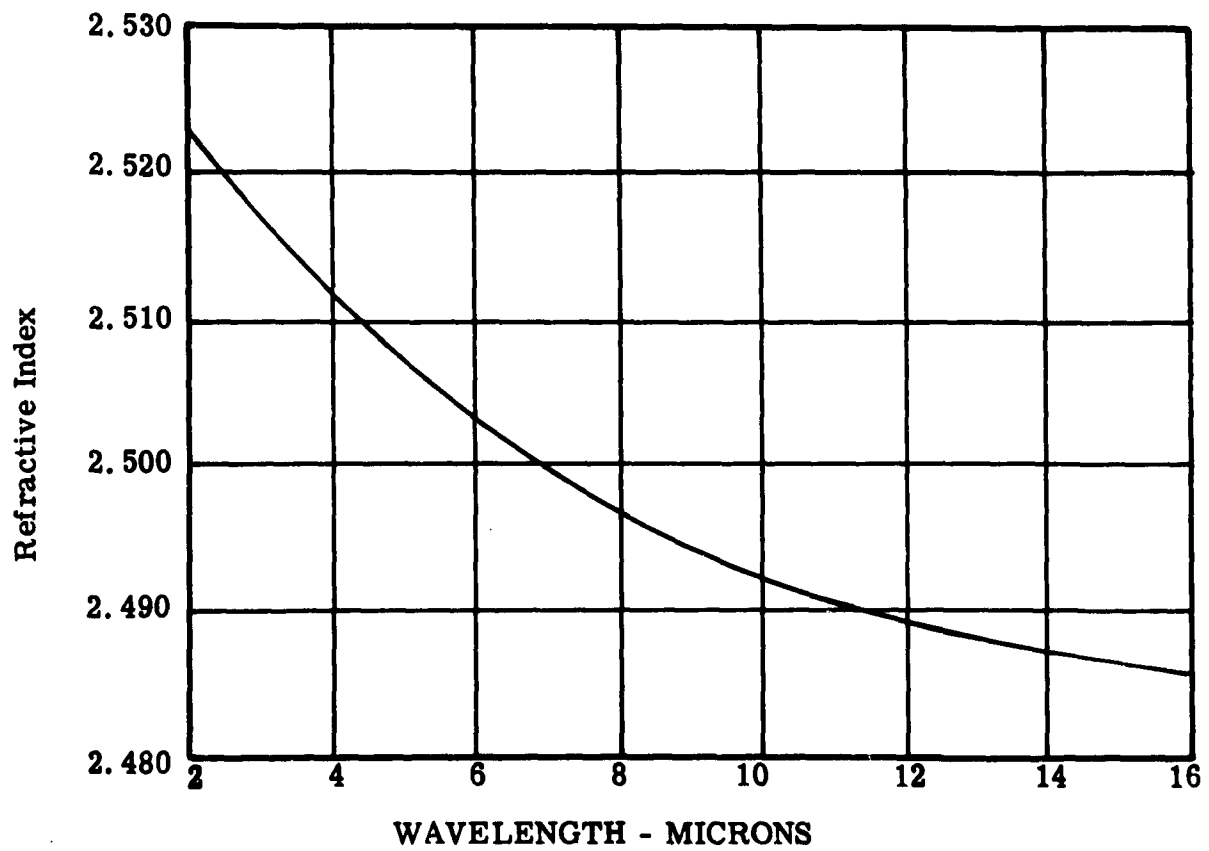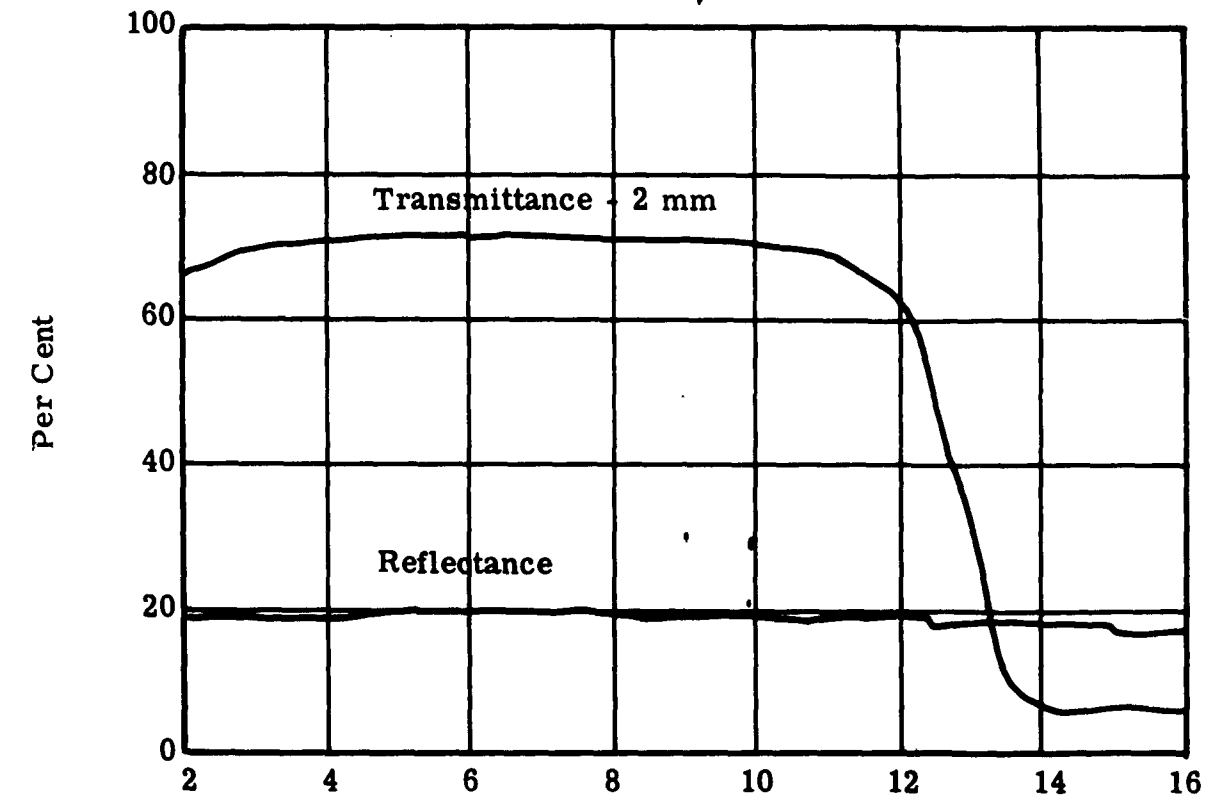
FIGURE 5.

OPTICAL PROPERTIES OF GLASS NO. A-161

WAVELENGTH - MICRONS

15
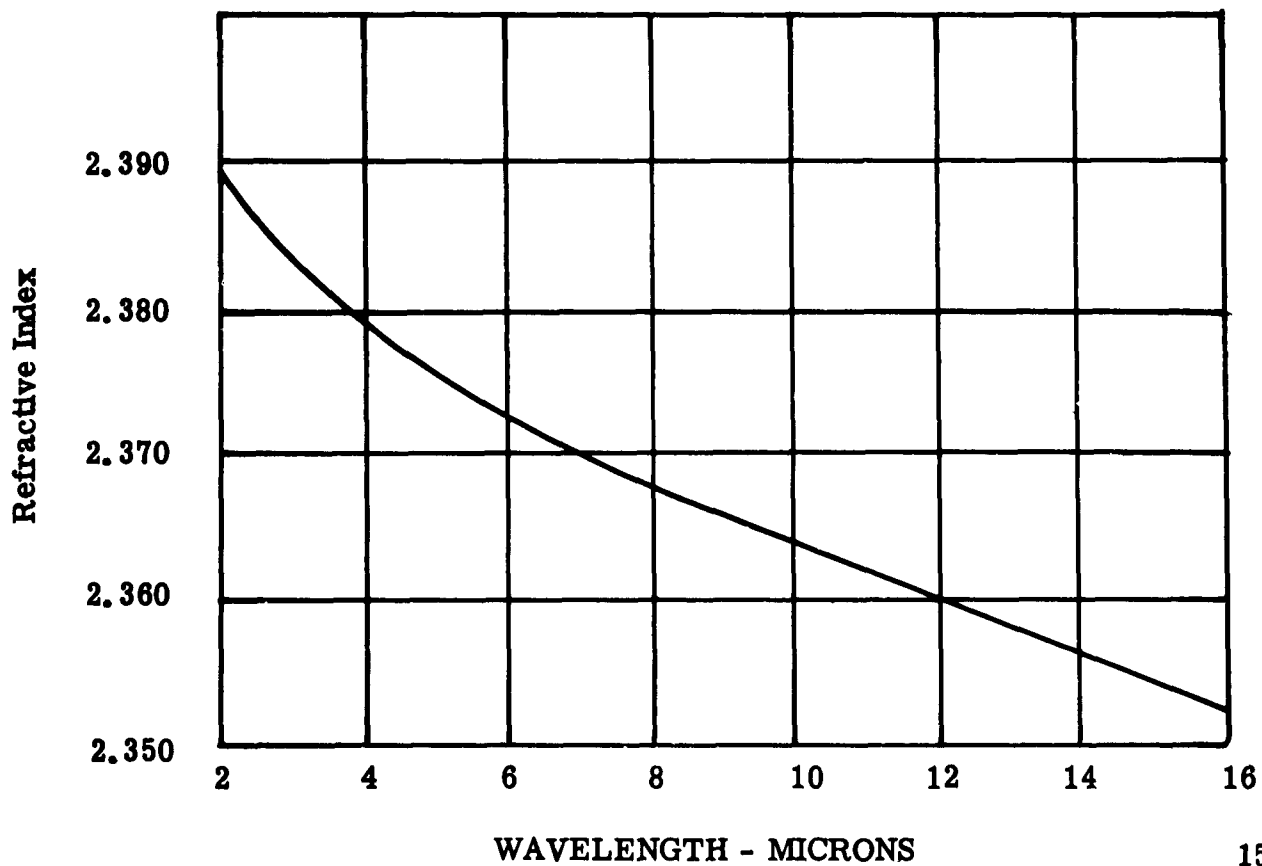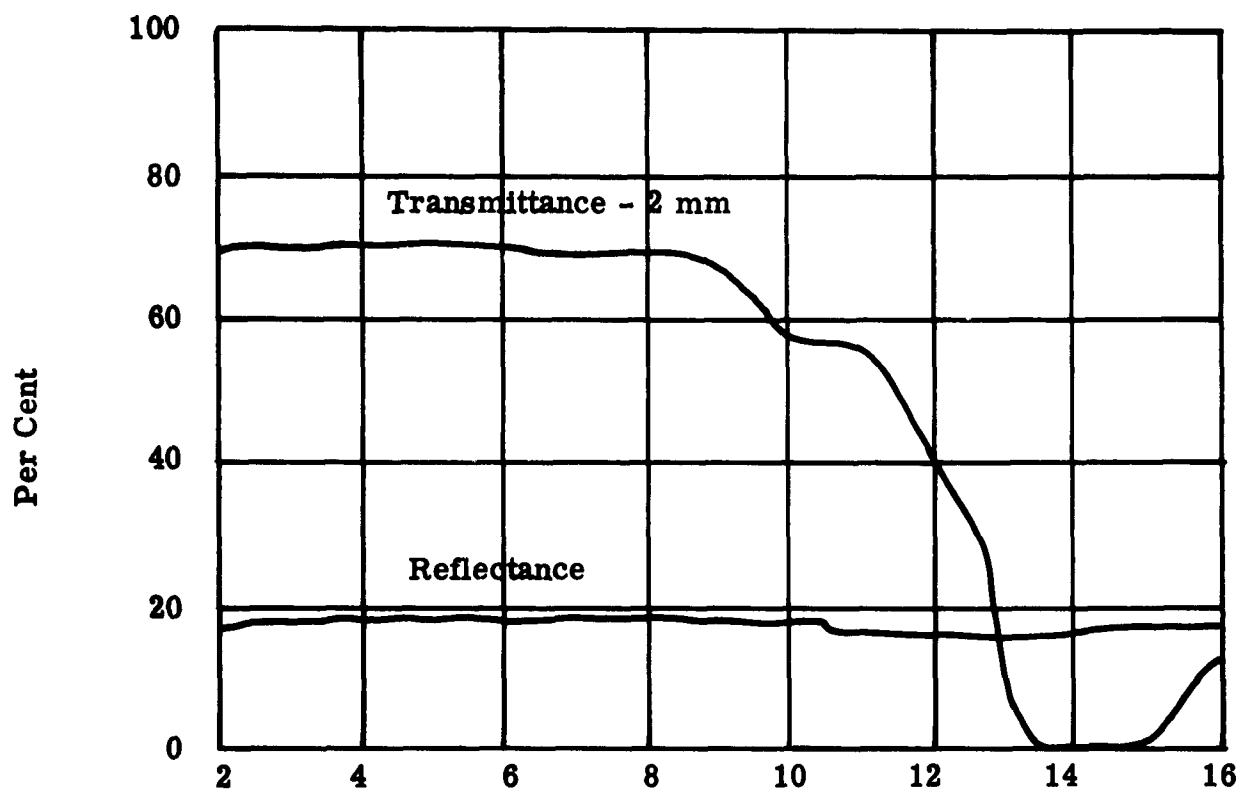
FIGURE 6.

OPTICAL PROPERTIES OF GLASS NO. A-166

WAVELENGTH - MICRONS

16
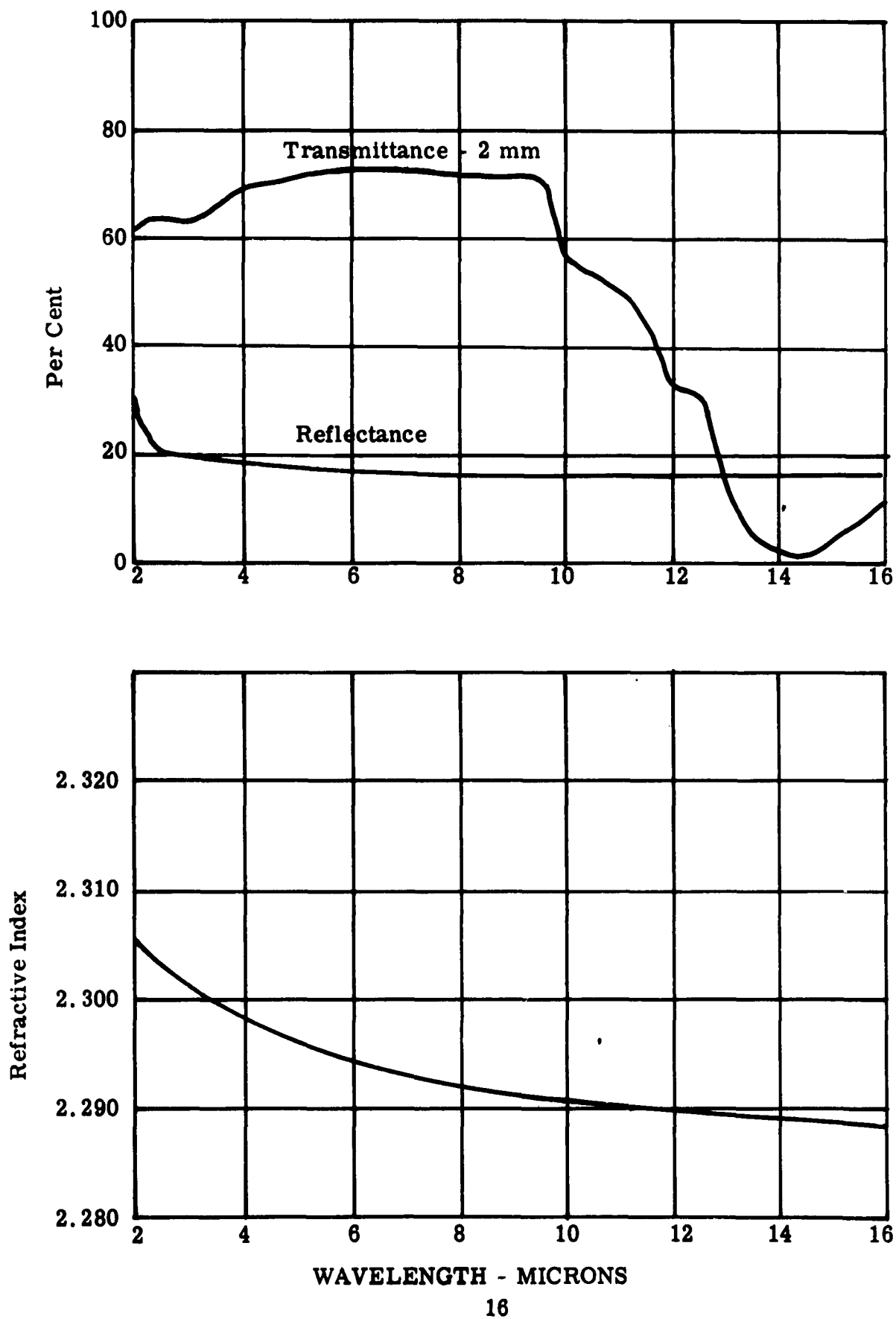
FIGURE 7.

OPTICAL PROPERTIES OF GLASS NO. A-174

WAVELENGTH - MICRONS

17
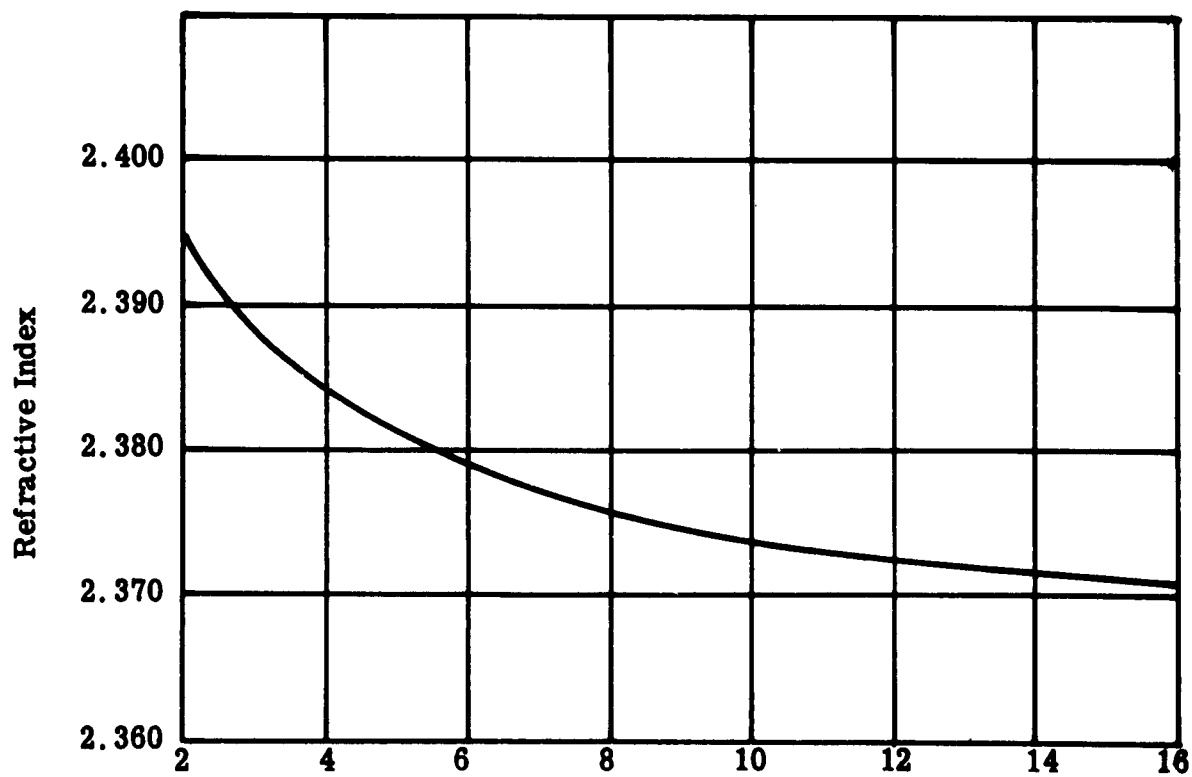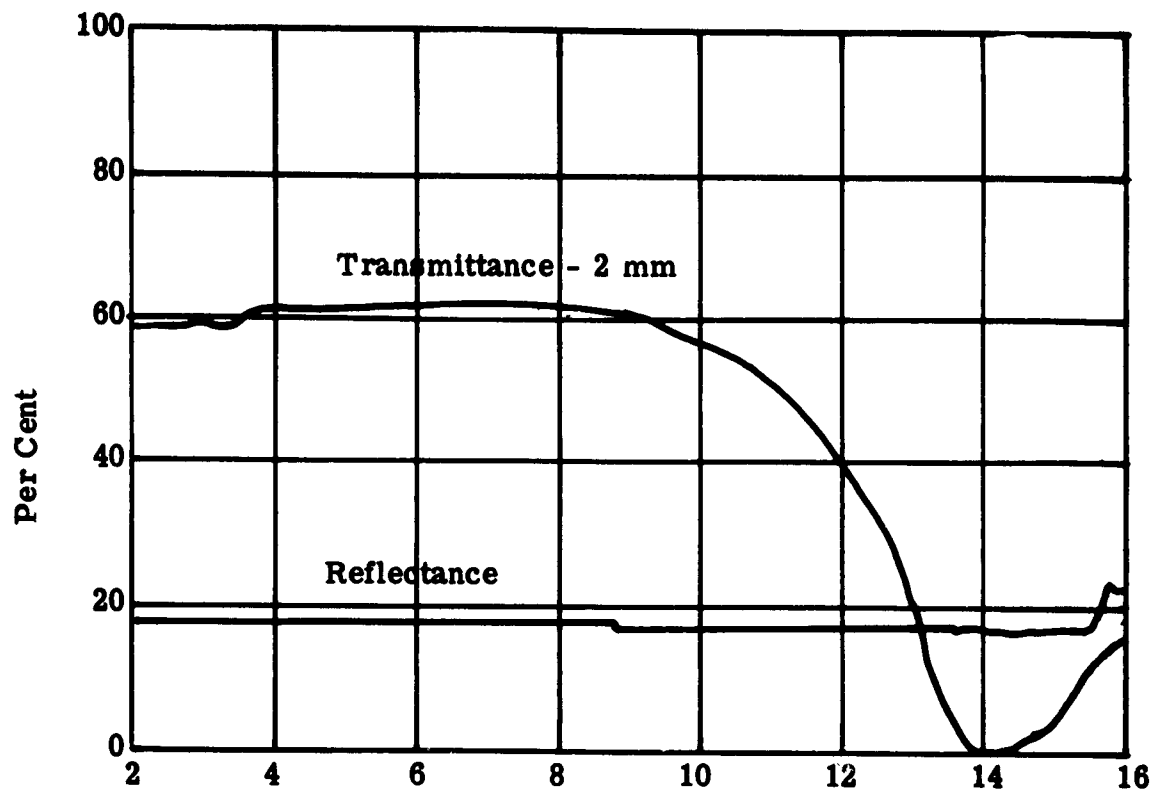
FIGURE 8.

OPTICAL PROPERTIES OF GLASS NO. A-215
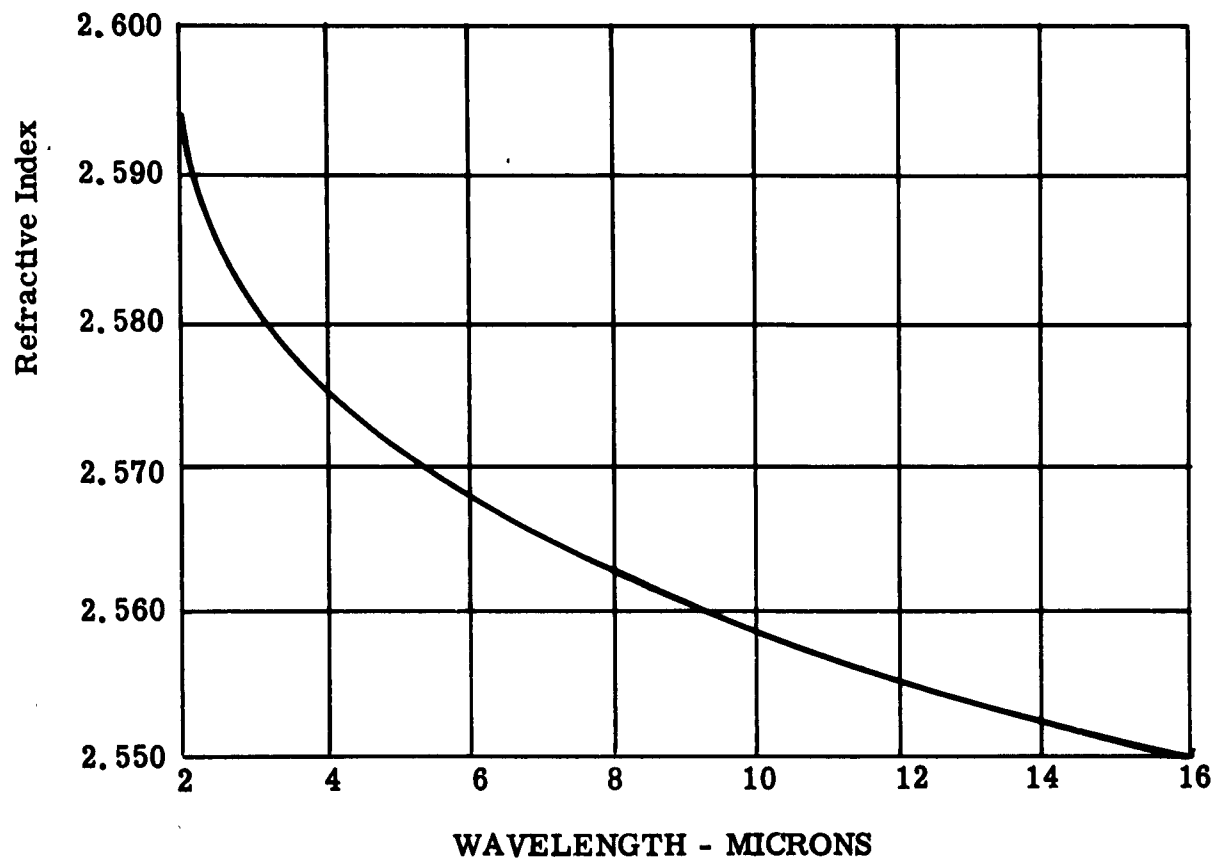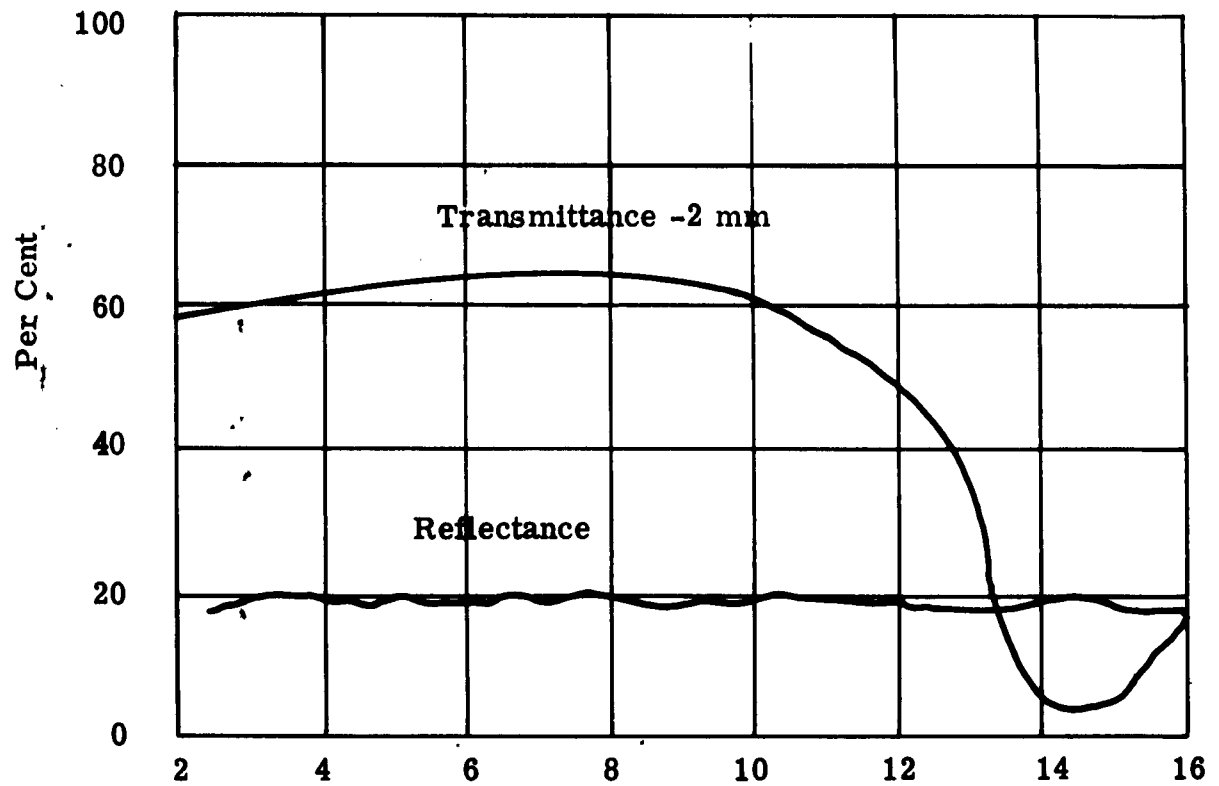
FIGURE 9.

OPTICAL PROPERTIES OF GLASS NO. A-216

WAVELENGTH - MICRONS
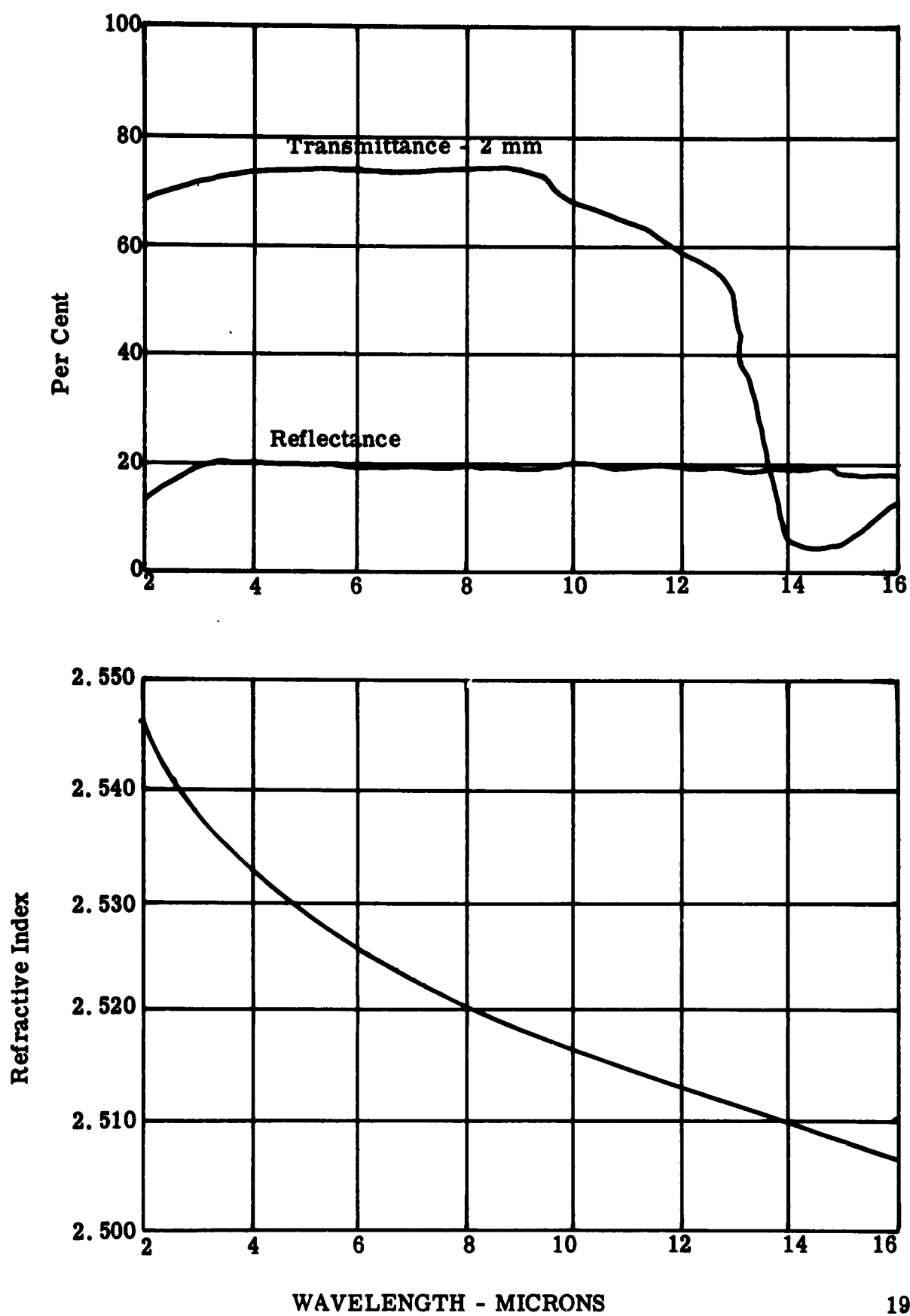
FIGURE 10.

OPTICAL PROPERTIES OF GLASS NO. A-218

WAVELENGTH - MICRONS

20
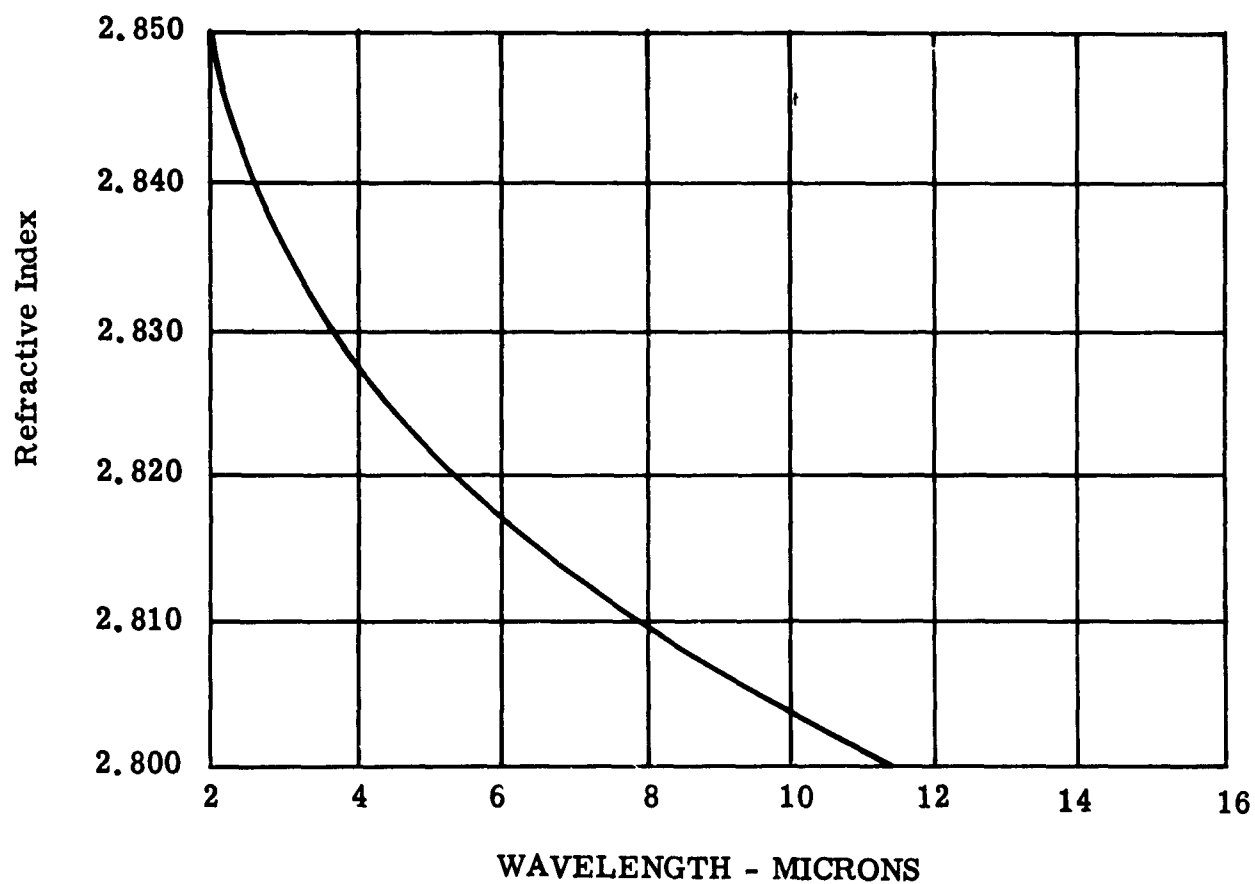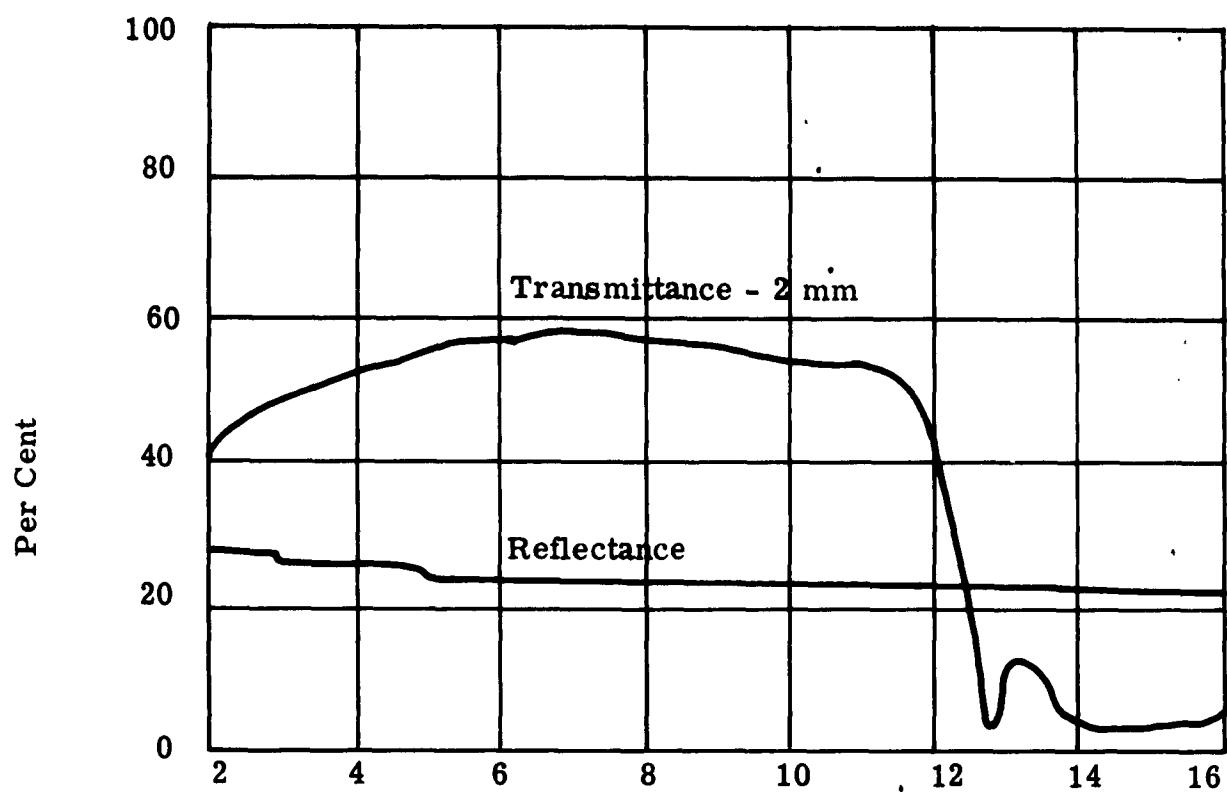
FIGURE 11.

OPTICAL PROPERTIES OF GLASS NO. 63-120
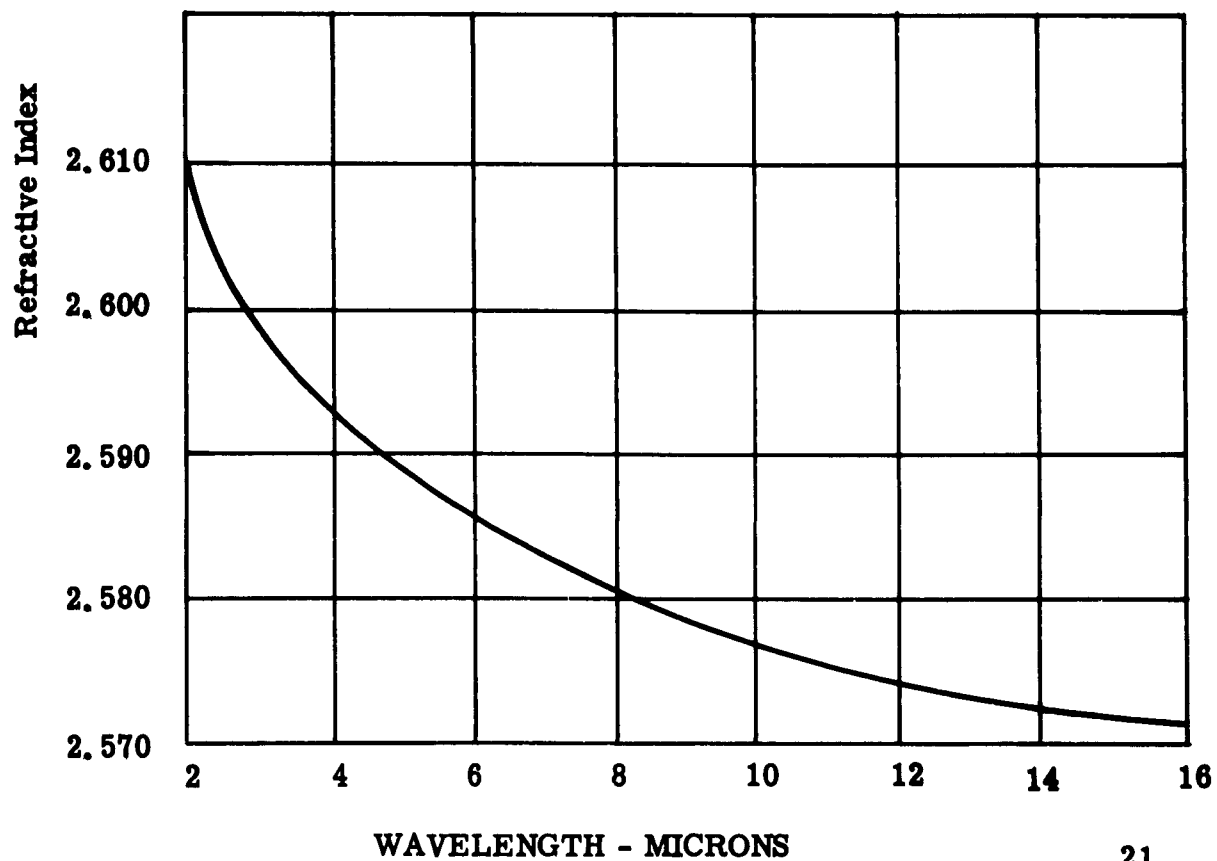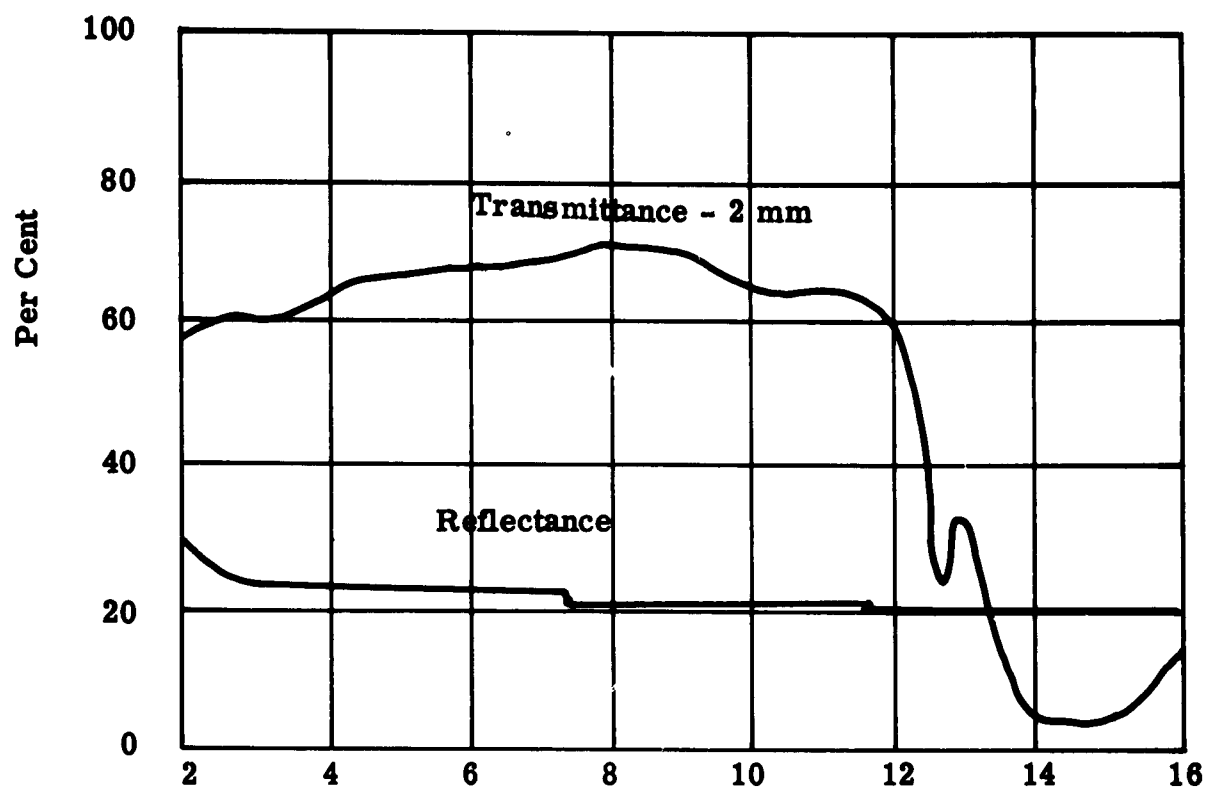
FIGURE 12.

OPTICAL PROPERTIES OF GLASS NO. 63-121

22
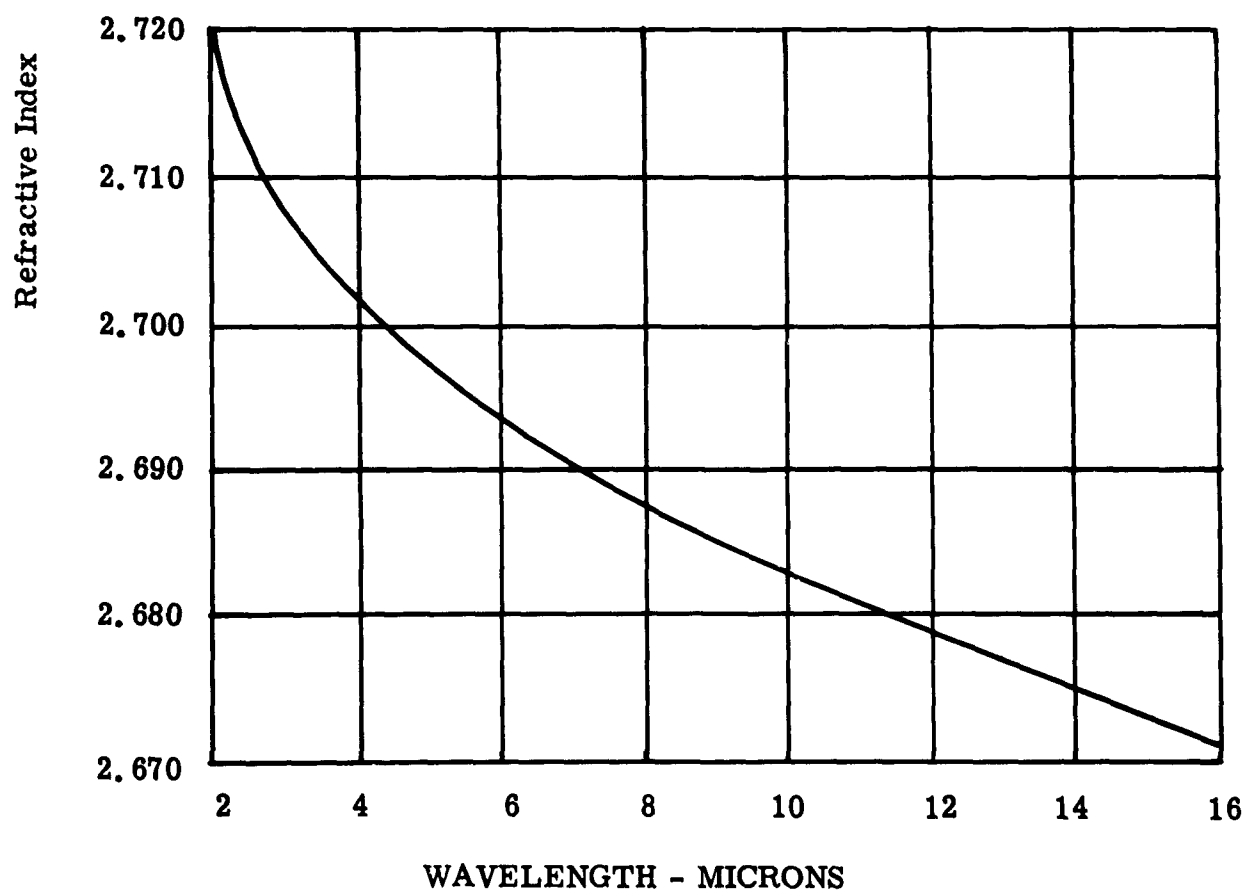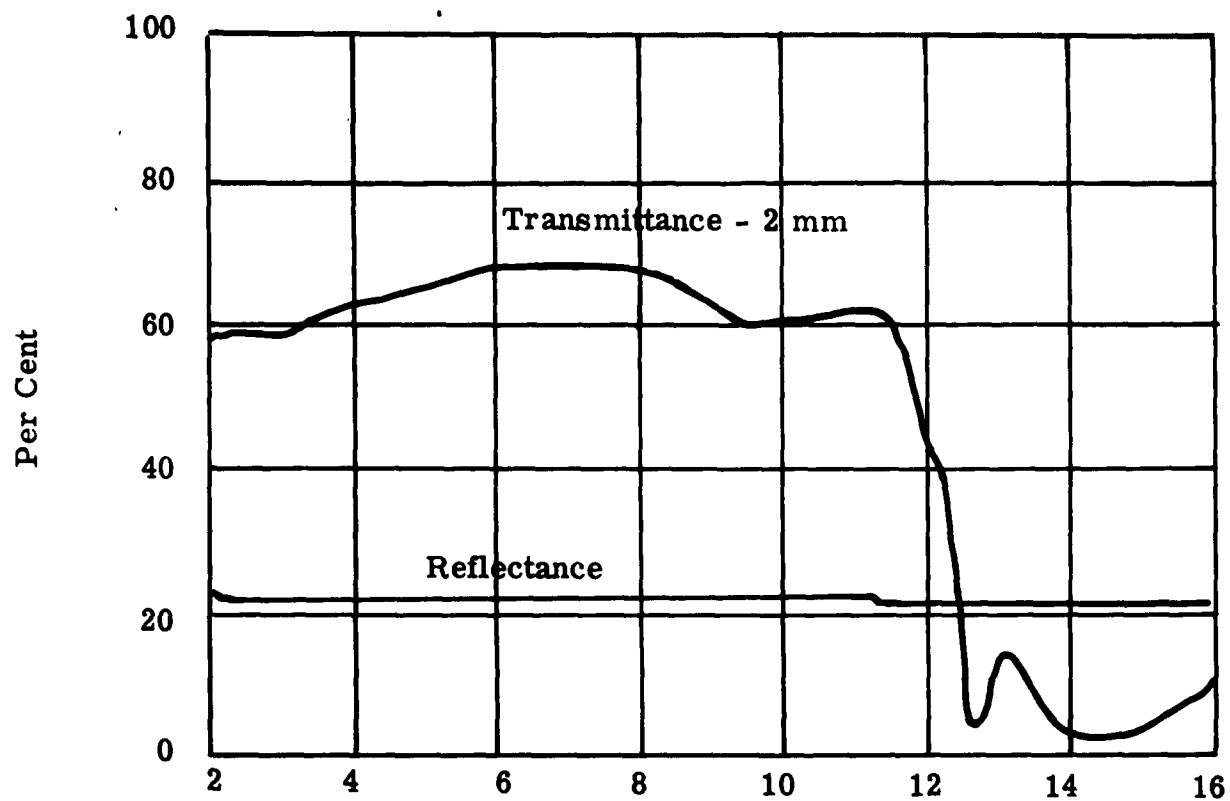
FIGURE 13.

OPTICAL PROPERTIES OF GLASS NO. 63-126

WAVELENGTH - MICRONS
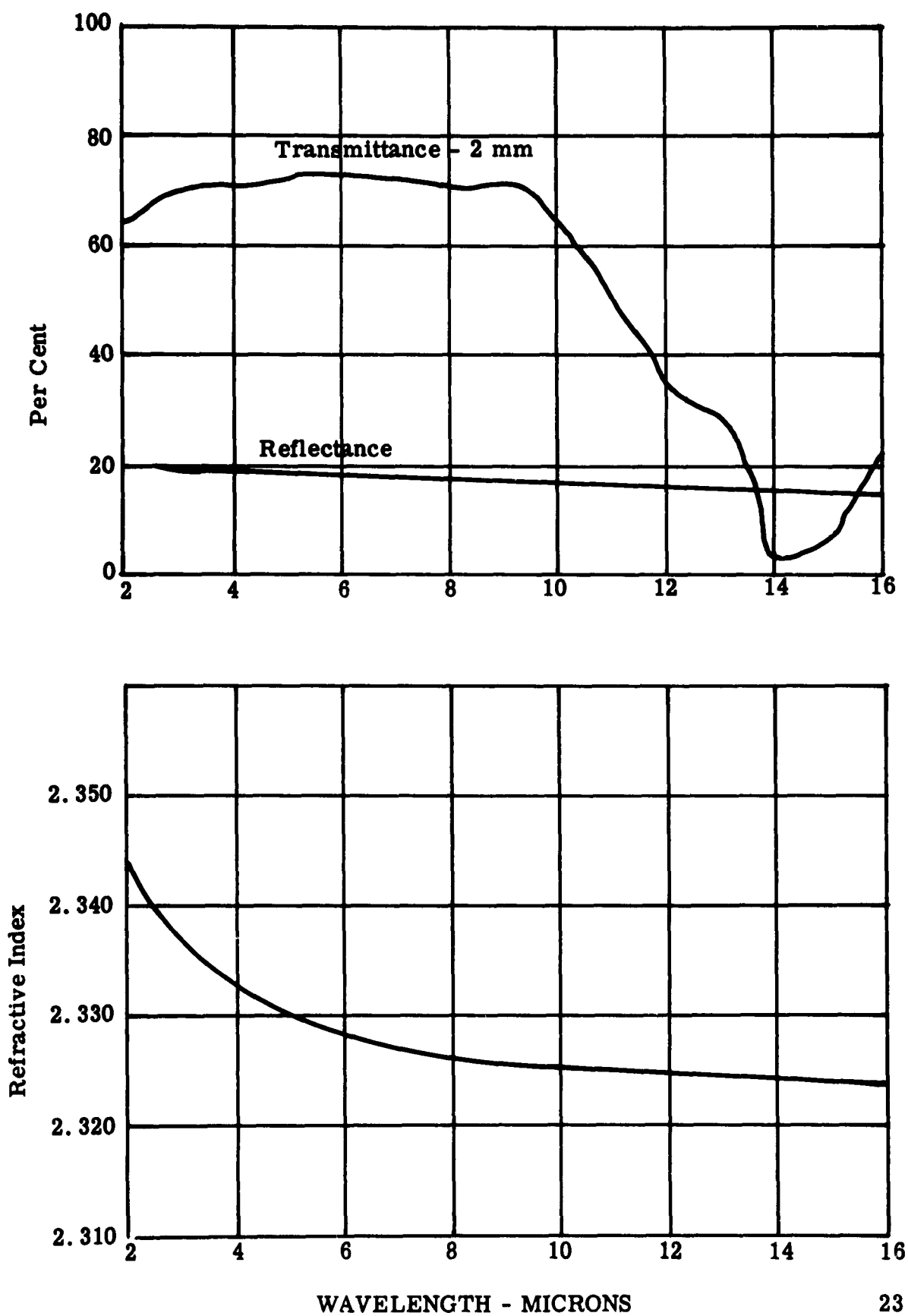
FIGURE 14.

OPTICAL PROPERTIES OF GLASS NO. 63-127

WAVELENGTH - MICRONS
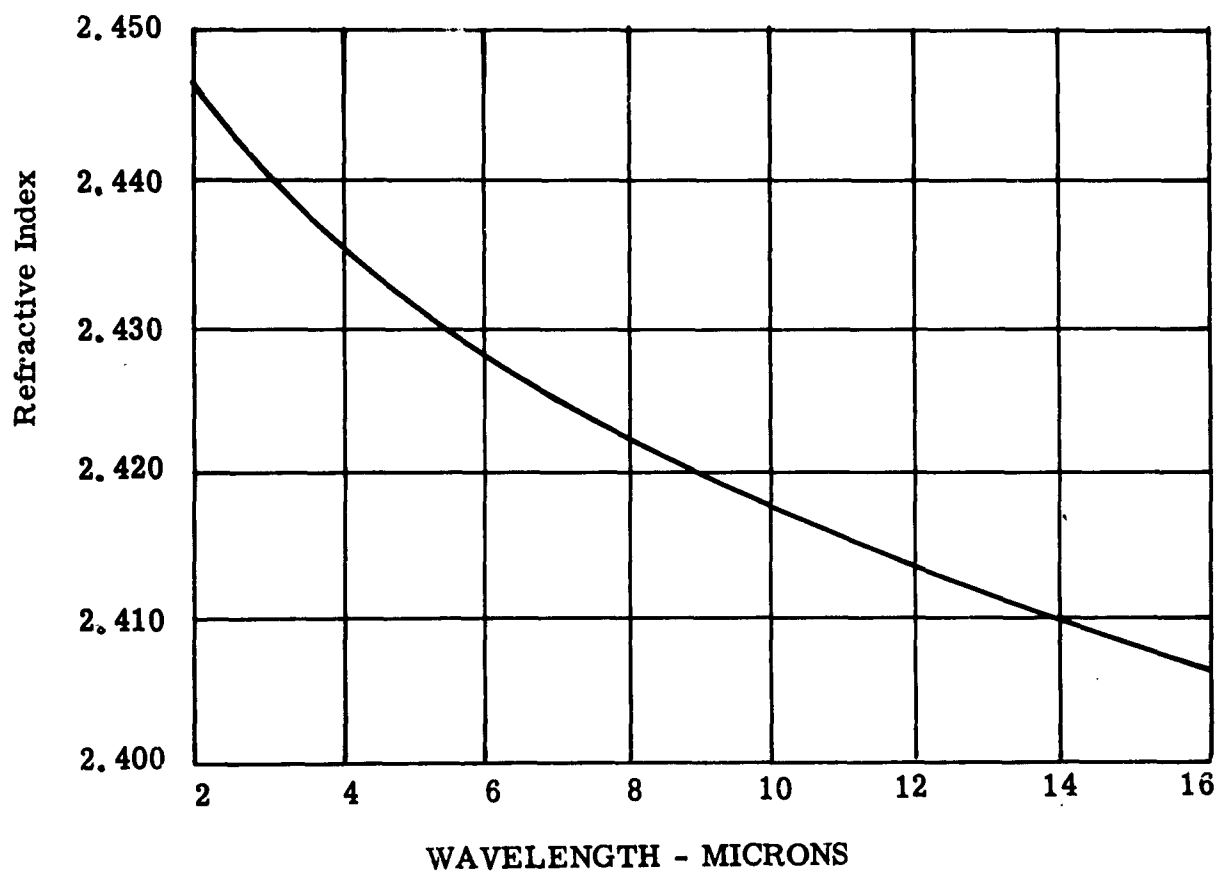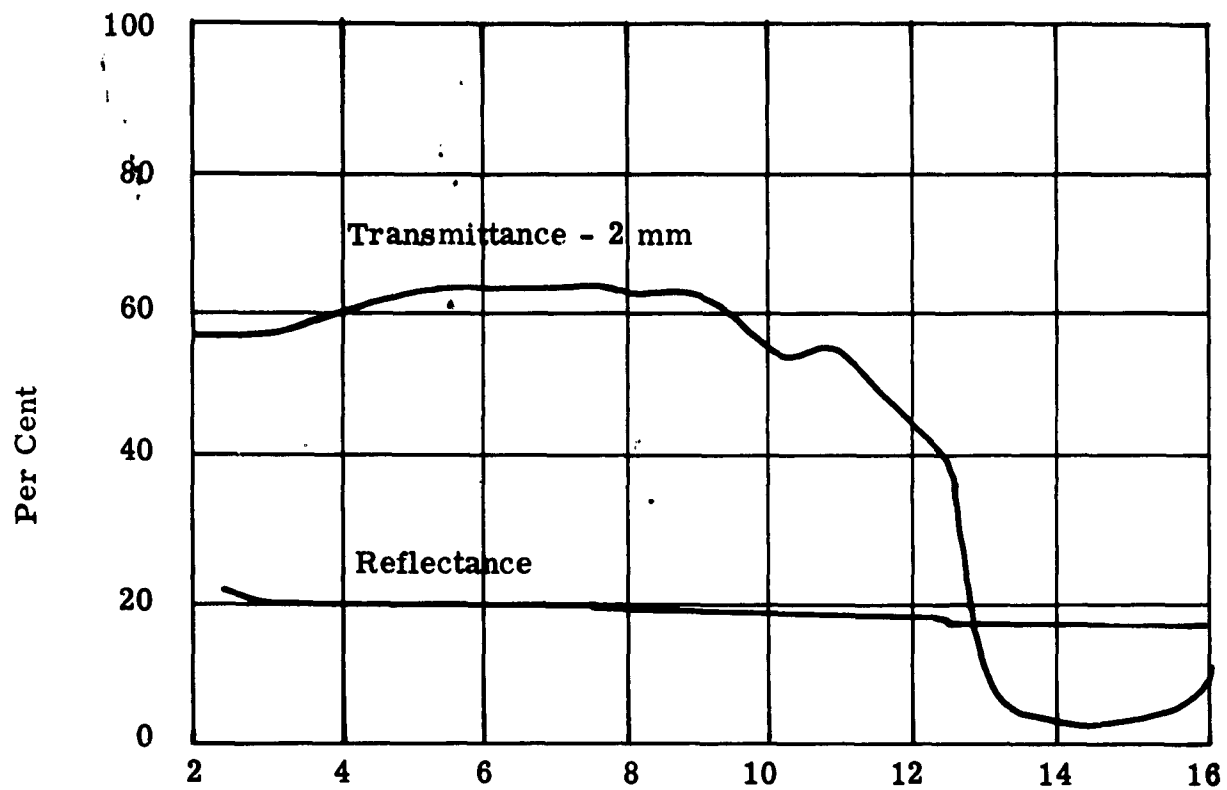
FIGURE 15.

OPTICAL PROPERTIES OF GLASS NO. 63-136

WAVELENGTH - MICRONS
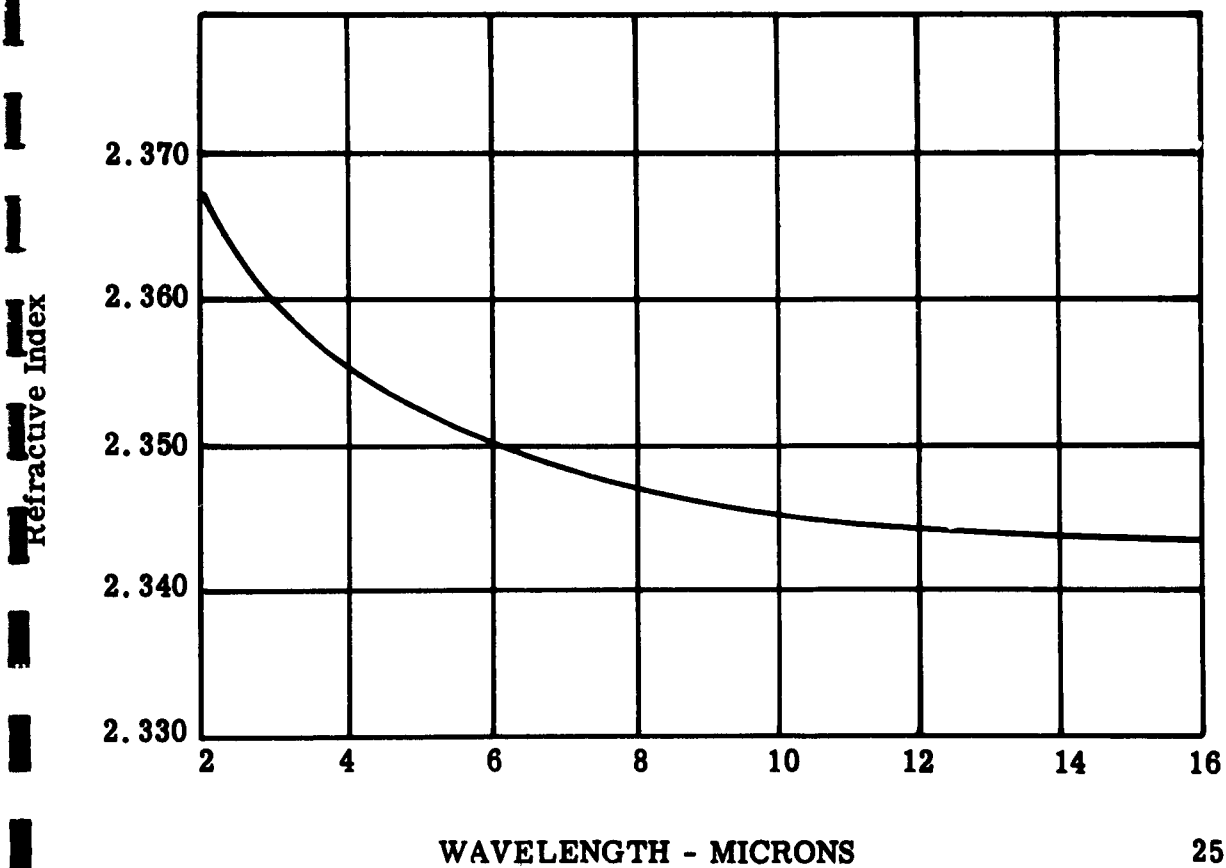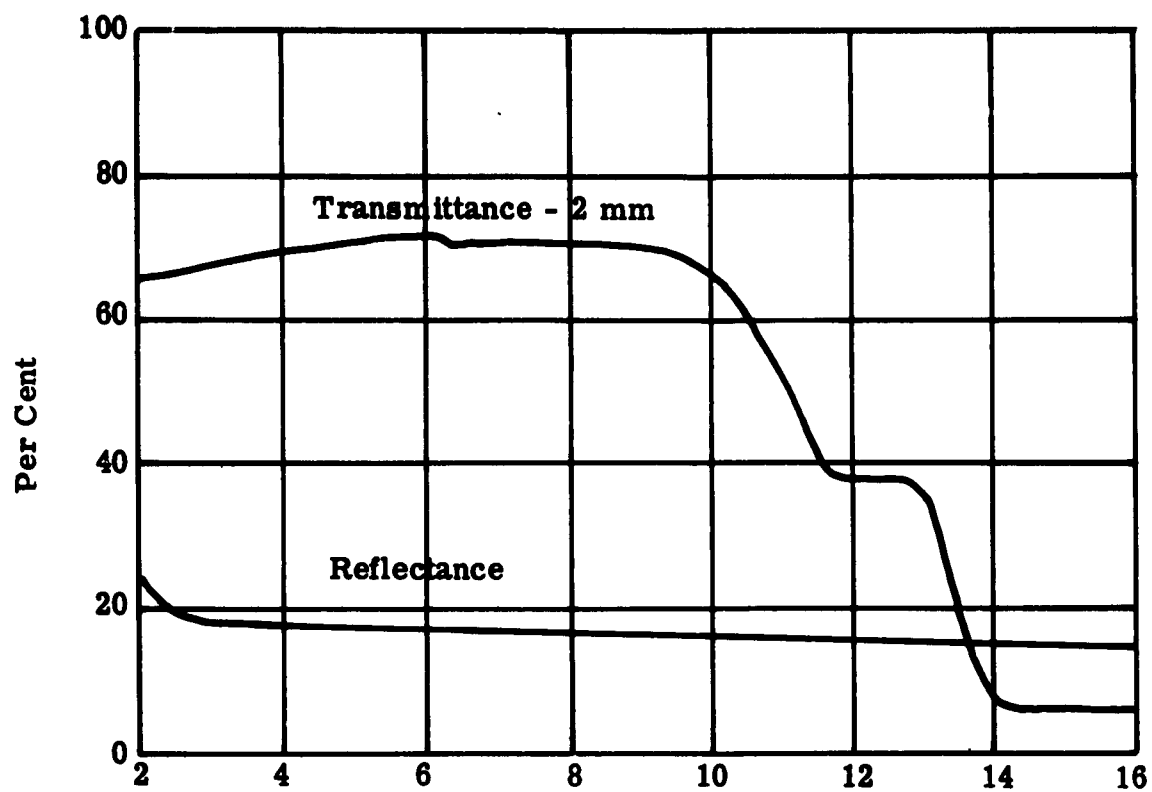
FIGURE 16.

OPTICAL PROPERTIES OF GLASS NO. 63-139

WAVELENGTH - MICRONS

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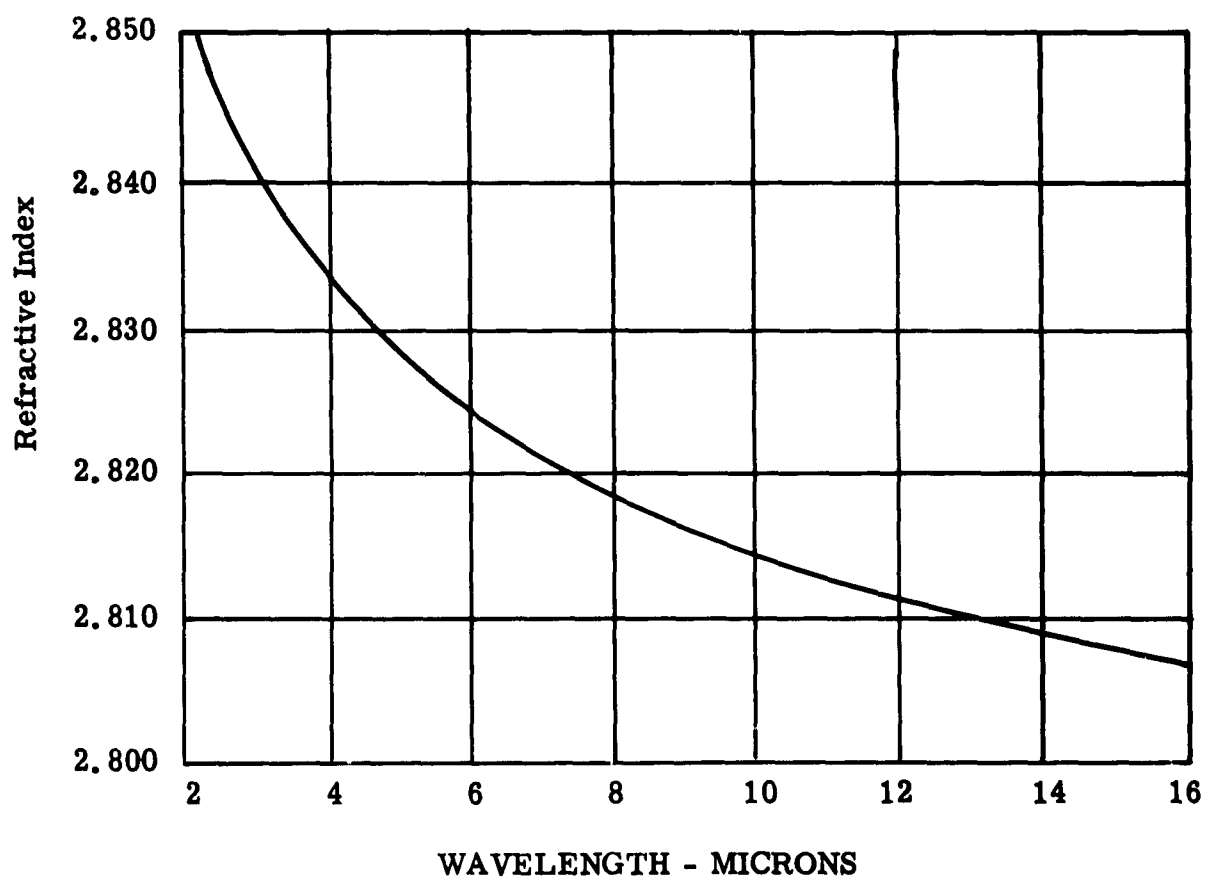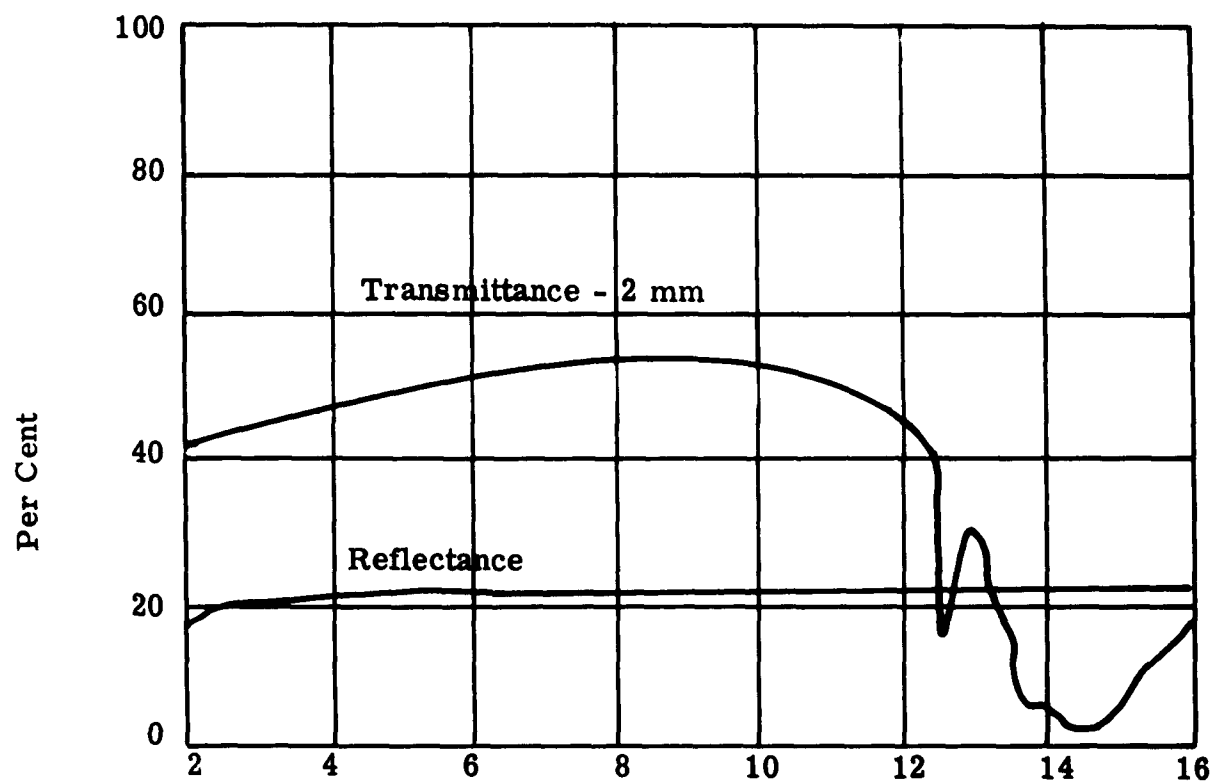
FIGURE   17.

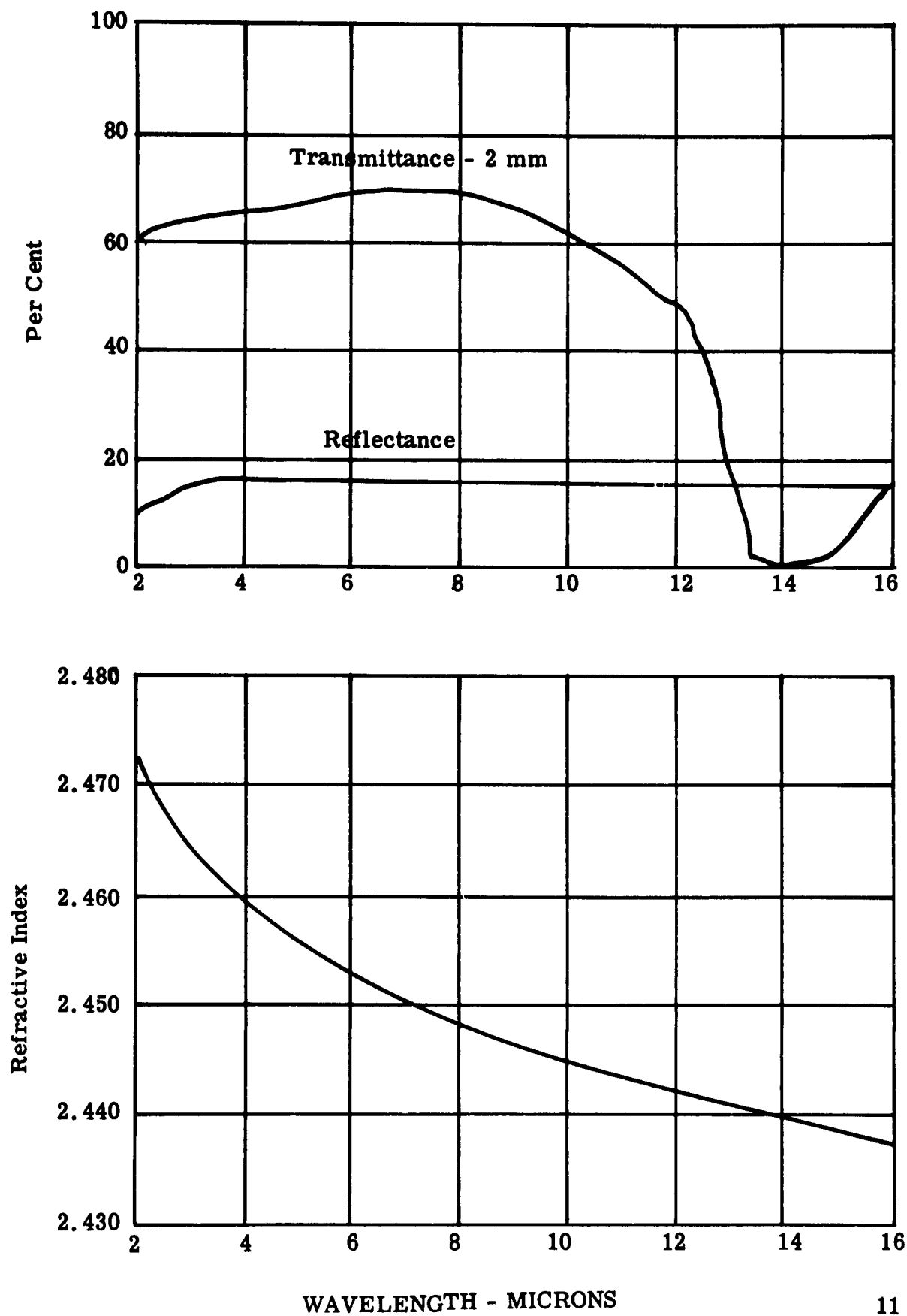## OPTICAL PROPERTIES OF GLASS NO. 63-145
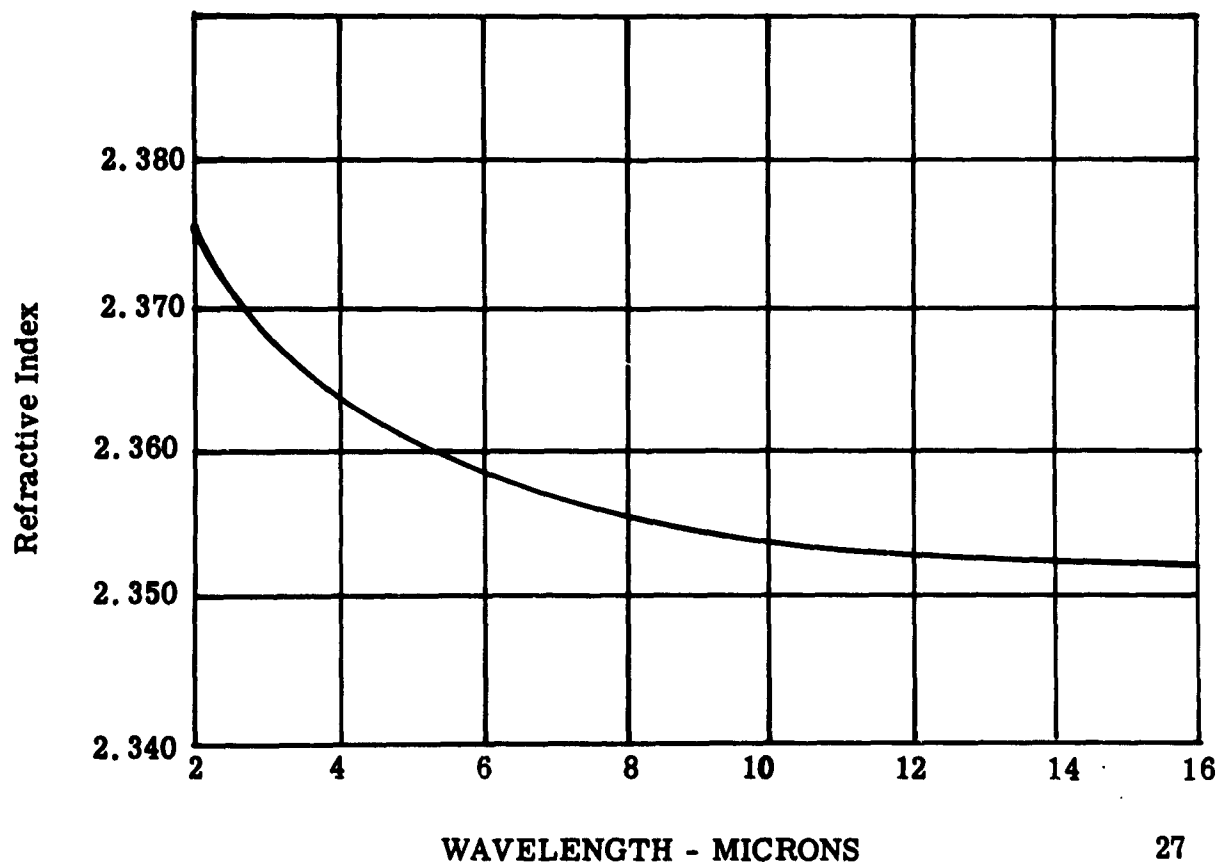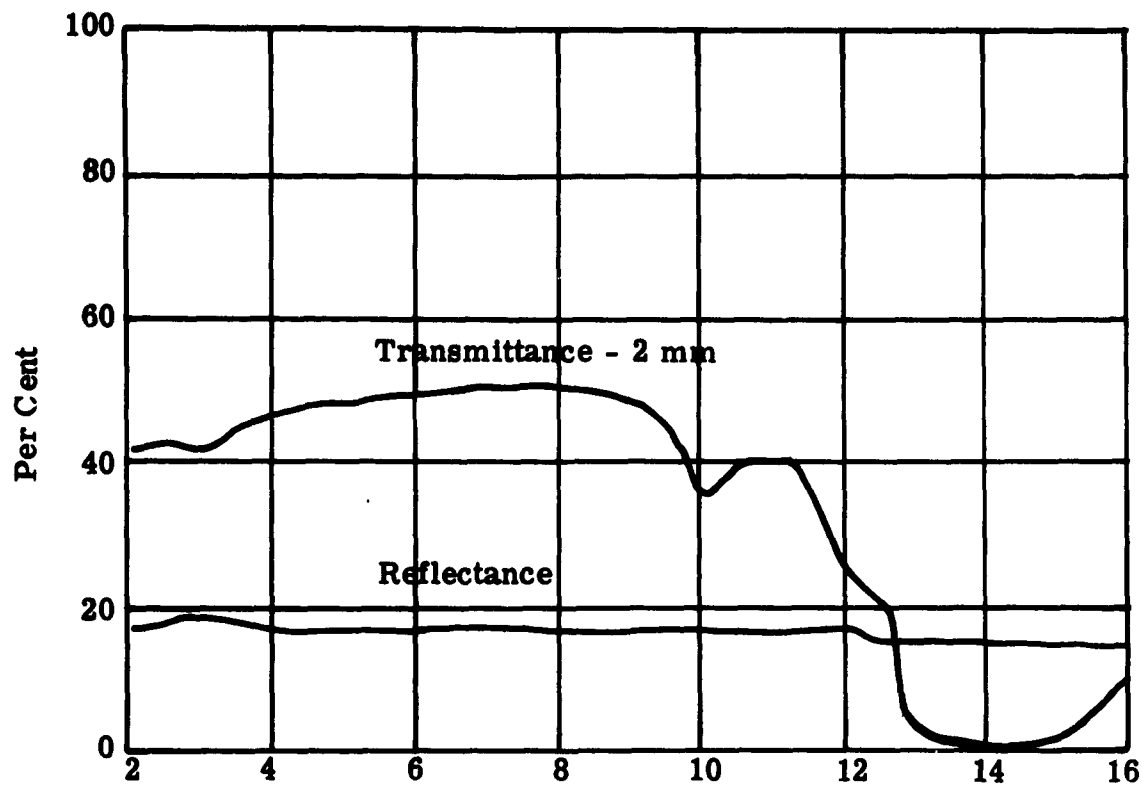
FIGURE 18.

OPTICAL PROPERTIES OF GLASS NO. 63-149
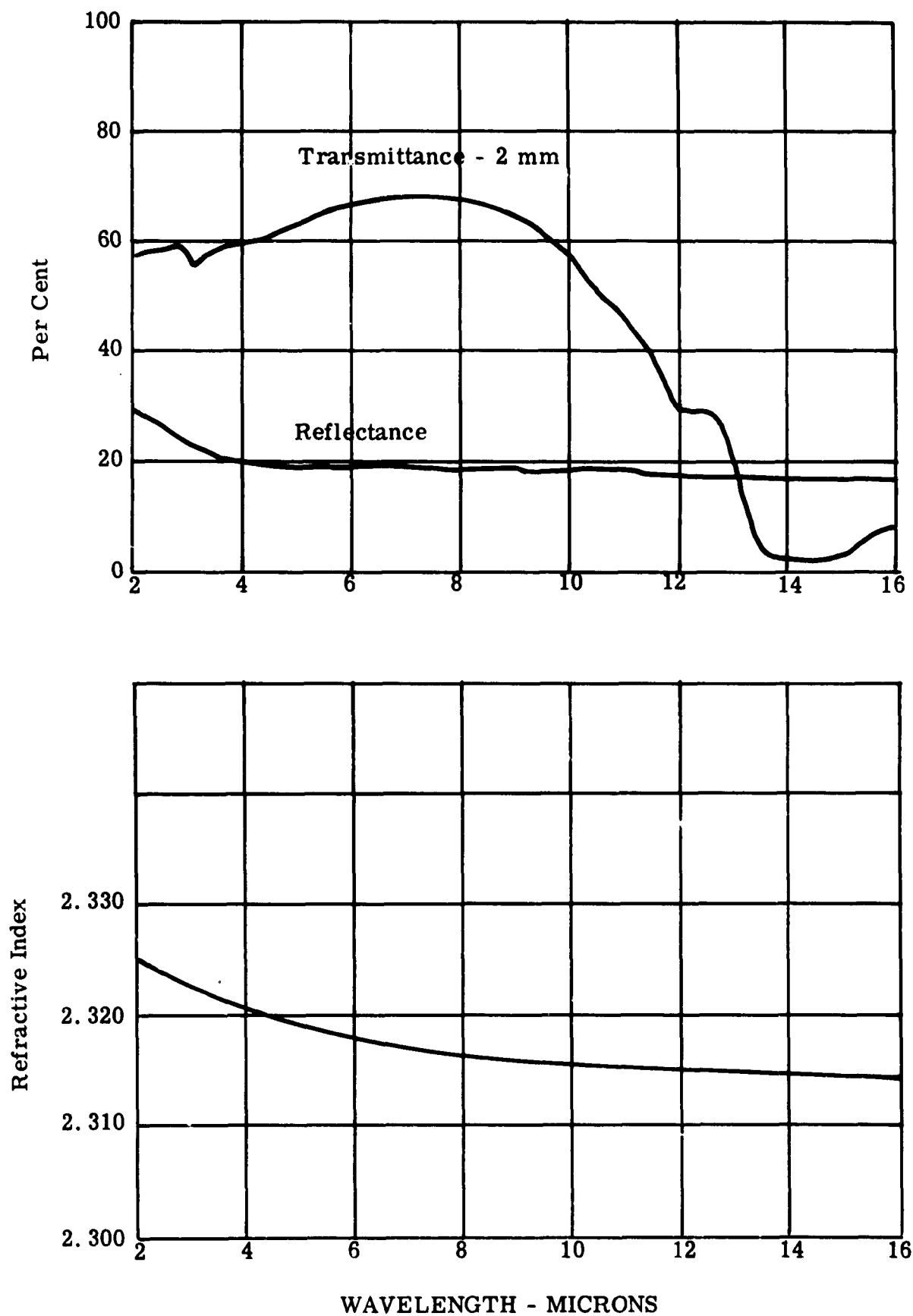
FIGURE   19.

OPTICAL PROPERTIES OF GLASS NO. 63-157

WAVELENGTH - MICRONS
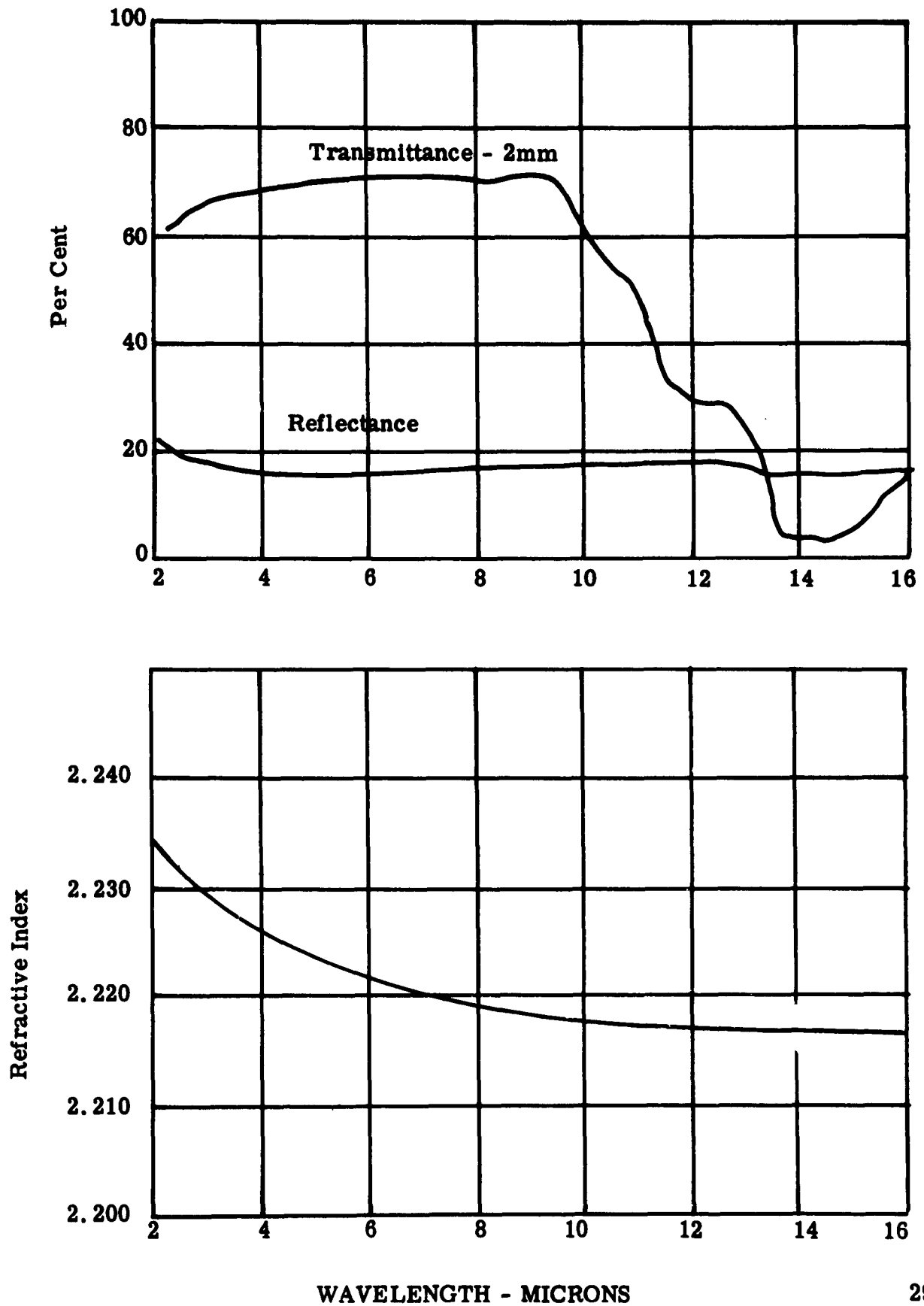
FIGURE   20.

OPTICAL PROPERTIES OF GLASS NO. 63-159
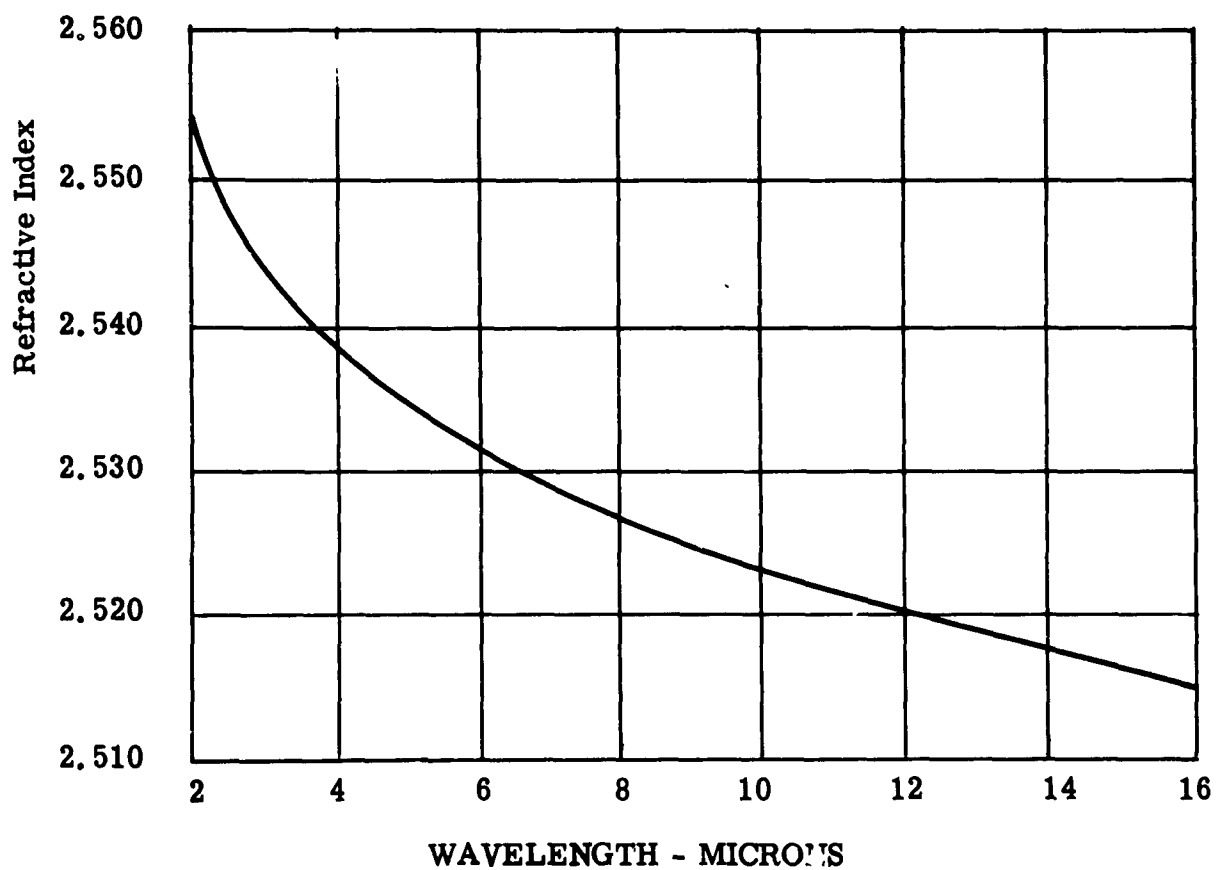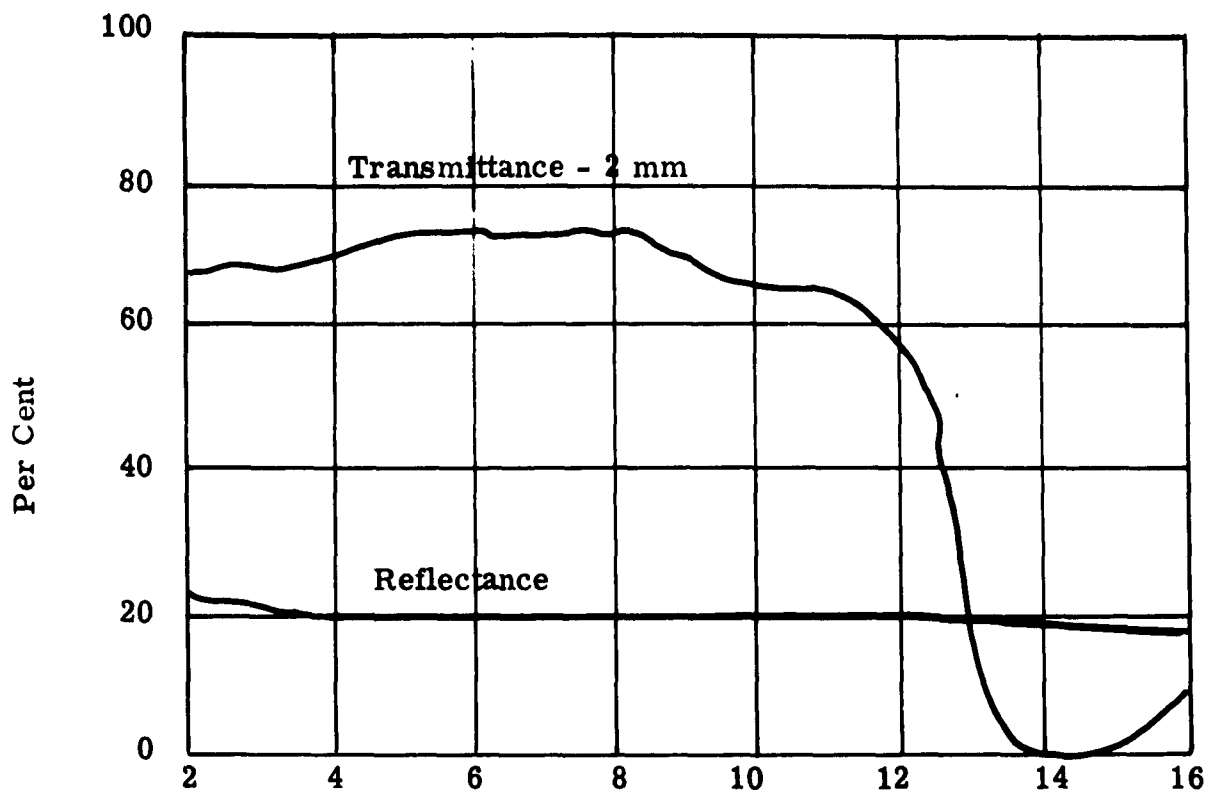
TABLE I

COMPOSITION OF SELECTED GLASSES (WEIGHT PERCENT)

GLASS NO.	As	S	Se	Te
A-21	40	20	40	-
A-22	20	20	60	-
A-145	40	5	45	10
A-160	50	20	20	10
A-161	40	30	20	10
A-166	40	40	10	10
A-174	30	30	20	20
A-215	15	15	30	40
A-216	20	20	20	40
A-218	30	10	20	40
63-120	25	10	45	20
63-121	35	10	35	20
63-126	20	30	30	20
63-127	40	30	10	20
63-136	20	30	20	30
63-139	20	5	35	40
63-145	50	40	-	10
63-149	30	40	-	30
63-157	30	40	30	-
63-159	50	20	30	-

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TABLE 2

THERMAL PROPERTIES OF SELECTED GLASSES

GLASS NO.	Thermal Exp x 10^{-6}/°C [3]	Critical Point-C°	Softening Point-C°	Thermal Cond x 10^{-4} Cal/sec cm C°	Specific Heat [1] Cal/gmC°	Rework ability [2]
A-21	28.5	105	156	4.62	.096	S
A-22	42.7	78	105	3.81	.105	S
A-145	21.9	165	189	4.74	.081	S
A-160	27.0	164	195	4.64	.092	S
A-161	27.6	111	172	4.36	.103	S
A-166	32.0	87	135	4.41	.110	S
A-174	32.6	90	134	4.03	.099	S
A-215	36.7	86	107	3.57	.081	S
A-216	29.7	80	121	4.28	.092	S
A-218	31.3	88	123	3.79	.078	P
63-120	30.6	86	117	4.09	.077	S
63-121	24.6	150	176	4.38	.075	S
63-126	37.2	101	137	3.82	.110	S
63-127	28.8	150	171	4.52	.119	S
63-136	35.1	85	107	3.53	.102	S
63-139	29.6	101	125	4.57	.067	P
63-145	20.2	151	177	4.61	.095	S
63-149	34.5	92	130	3.69	.110	P
63-157	50.0	95	113	3.92	.121	S
63-159	20.3	151	218	4.33	.101	S

1. Average Temperature, 40°C

2. S-Satisfactory
   P-Poor

3. 25°C to Critical Point

TABLE 2A

GLASSES IN ORDER OF SOFTENING TEMPERATURE

GLASS NO.	SOFTENING POINT C°	CRITICAL POINT C°
63-159	218	151
A-160	195	164
A-145	189	165
63-145	177	151
63-121	176	150
A-161	172	111
63-127	171	150
A21	156	105
63-126	137	101
A-166	135	87
A-174	134	90
63-149	130	92
63-139	125	101
A-218	123	88
A-216	121	80
63-120	117	86
63-157	113	95
A-215	107	86
63-136	107	85
A-22	105	78

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TABLE 3

CHEMICAL DURABILITY OF SELECTED GLASSES

WEIGHT LOSS - GRAMS PER SQUARE INCH

Glass No.	H₂O 25°C	H₂O 90°C	NH₄OH 60°C	KOH 60°C	HCL 60°C	HNO₃ 60°C	H₂SO₄ 60°C	ETHYL ALCOHOL 60°C
A-21	0	0	.046	.578	0	0	0	0
A-22	0	0	.443	.604	0	0	0	0
A-145	0	0	0	.696	0	0	0	0
A-160	0	0	.030	.651	0	0	0	0
A-161	0	0	.534	.532	0	0	0	0
A-166	0	0	.745	.357	0	0	0	0
A-174	0	0	.195	.413	0	0	0	0
A-215	0	0	.133	.621	.001	.002	0	0
A-216	0	.002	.279	.478	0	.001	0	0
A-218	0	0	.002	.662	0	0	0	0
63-120	0	0	.012	.475	0	0	0	0
63-121	0	0	.005	.662	0	0	0	0
63-126	0	0	.045	.486	0	0	0	0
63-127	0	0	.142	.465	0	0	0	0
63-136	0	.001	.192	.420	0	0	0	.003
63-139	0	0	.018	.704	.001	0	0	0
63-145	0	0	.198	.467	0	0	0	0
63-149	0	.001	.164	.396	0	0	0	.001
63-157	0	0	.108	.377	0	0	0	0
63-159	0	0	.017	.594	0	0	0	0

Concentration of Reagents Used

NH₄OH	.3 Normal	HNO₃	1.1 Normal
KOH	.4 Normal	H₂SO₄	2.1 Normal
HCL	1.0 Normal	Ethyl Alcohol 90% Volume	

Test: Samples soaked for 6 hours at temperature shown in 10 ml of reagent

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TABLE 4

ELECTRICAL PROPERTIES OF SELECTED GLASSES

Glass No.	Dielectric Constant, 1 MC	Resistivity ohm cm x 10^{10}
A-21	6.99	20.
A-22	5.77	21.
A-145	6.57	3.2
A-160	7.68	19.
A-161	6.50	16.
A-166	6.04	30.
A-174	6.33	25.
A-215	7.35	1.9
A-216	8.06	3.9
A-218	5.78	0.012
63-120	7.11	9.4
63-121	8.20	1.7
63-126	5.89	17.
63-127	6.86	26.
63-136	5.99	22.
63-139	14.31	0.023
63-145	6.46	28.
63-149	6.47	31.
63-157	5.51	25.
63-159	7.35	20.

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TABLE 5

PHYSICAL PROPERTIES OF SELECTED GLASSES

Glass No.	Knoop Hardness	Young's Modulus psi x 10^6	Tensile Strength psi	Compressive Strength psi	Specific Gravity
A-21	91	2.16	2670	19390	3.56
A-22	54	1.14	1950	14300	3.53
A-145	114	2.41	2540	17710	4.43
A-160	94	1.46	1850	18340	3.67
A-161	89	1.86	3400	2210	3.35
A-166	76	1.67	2550	15780	3.18
A-174	71	1.68	3180	15600	3.38
A-215	71	2.06	2160	12870	4.07
A-216	79	1.12	1930	13220	3.88
A-218	106	2.20	2720	6900	4.40
63-120	91	1.55	1850	4100	4.17
63-121	106	2.55	4380	16780	4.23
63-126	49	1.21	1840	6670	3.33
63-127	97	2.00	3960	10590	3.38
63-136	60	1.37	1980	10000	3.41
63-139	103	1.25	1780	3780	4.64
63-145	92	2.69	4170	11180	3.08
63-149	70	1.36	2540	8820	3.19
63-157	57	1.16	2120	12210	3.02
63-159	121	2.14	2720	7470	3.65

5. **Discussion of Results**

The following is a discussion of the various properties the glasses and their significance as related to composition.

5.1 **Optical Properties**

5.1.1 **Infrared Transmission**

Transmission of most of the glasses were quite similar particularly with respect to cut-off wavelength. The five glasses having the lowest sulfur content, however, had somewhat better long wavelength transmission. This is in agreement with previous determinations that sulfur is the transmission limiting constituent.

5.1.2 **Infrared Reflectance**

The reflectance curves are generally in agreement with the index of refraction values (n) of 2.2 to 2.8 according to the formula;

$$\text{Reflectance} = \left(\frac{n-1}{n+1}\right)^2$$

5.1.3 **Index of Refraction**

The overall range among the 20 glasses extends from about 2.2 to 2.8 which affords a significant range for the design of highly corrected multi-element refractive systems.

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Figure 21 shows that the index of refraction varies directly as specific gravity (ρ) and that a good approximation of refractive index can be calculated using the equation;

$$N = \frac{5\rho}{12} + .98 \text{ for glasses in the field As-S-Se-Te.}$$

Figure 22 shows that the index of refraction of As-S-Se-Te glasses varies inversely with the specific heat (C) and from this the index can also be approximated using the equation;

$$N = -9.41 C + 3.37$$

5.2 Thermal Properties

5.2.1 Specific Heat

For the 20 glasses measured, the mean value of specific heat is low in comparison with silicate glasses, e.g. fused silica is 0.18 and ordinary window glass is 0.16 in this temperature range. Since index of refraction varies directly as specific gravity and inversely as specific heat, Figures 21 and 22, the specific heat varies inversely as specific gravity.

Addition of sulfur (highest in specific heat) produces an increase in specific heat and addition of tellurium (lowest in specific heat) causes a reduction in specific heat.
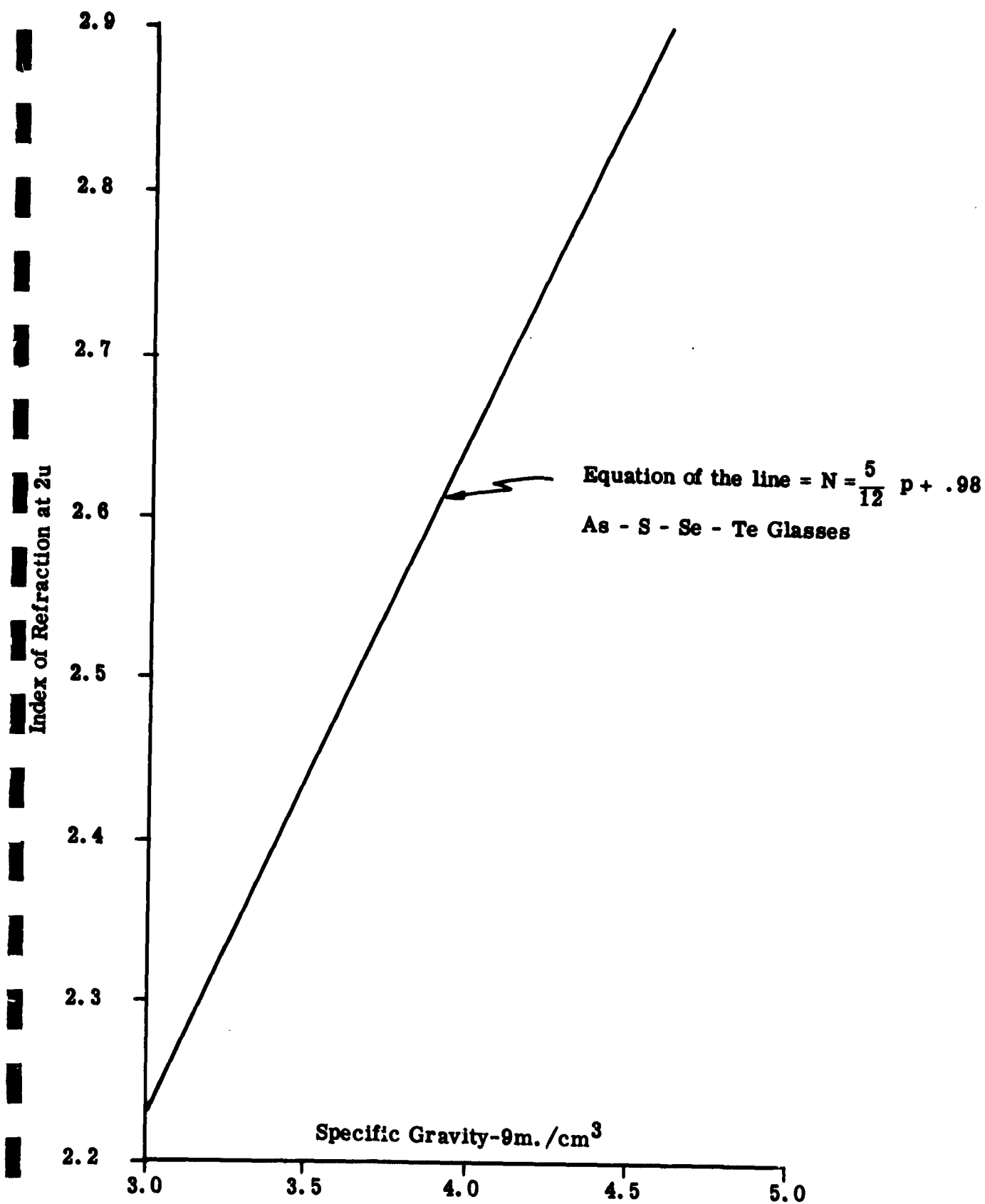
Figure 21. Index of Refraction at 2 Microns vs. Specific Gravity

The y-axis is labeled "Index of Refraction at 2u" with values 2.2, 2.3, 2.4, 2.5, 2.6, 2.7, 2.8, 2.9.

The x-axis is labeled "Specific Gravity-9m./cm^3" with values 3.0, 3.5, 4.0, 4.5, 5.0.

Equation of the line = $N = \frac{5}{12} p + .98$

As - S - Se - Te Glasses
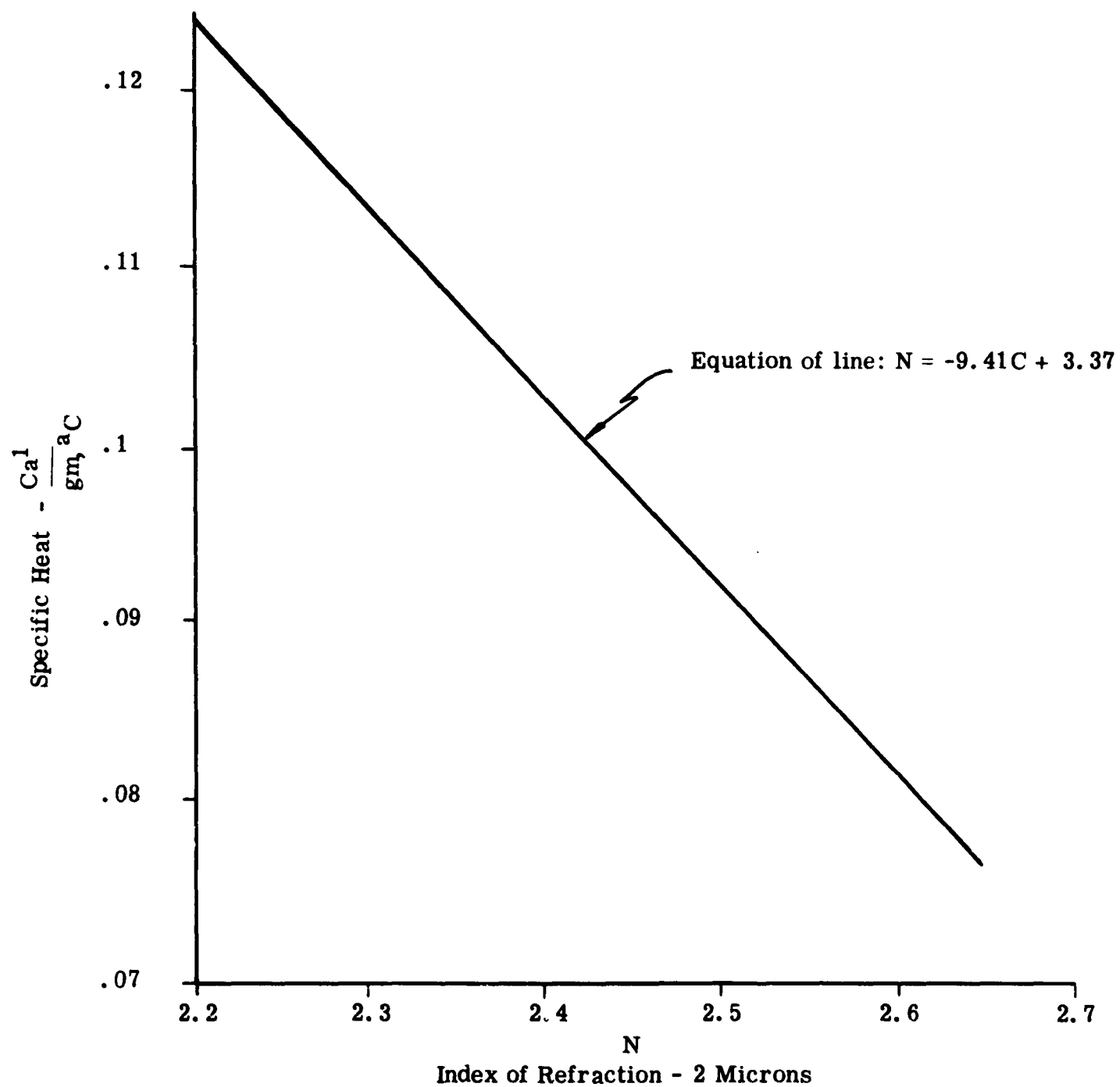
Figure 22.   Specific Heat vs. Index of Refraction

5.2.2   Thermal Conductivity

Thermal conductivity appears to vary with composition in the
same manner as the softening and critical points. Glasses that
have highest thermal conductivities also have highest softening
temperature.

5.2.3   Softening Point

Softening temperature varies exponentially with the arsenic content
keeping the content of tellurium constant as shown in Figure 23.
This is true whether arsenic replaces sulfur or selenium.

5.2.4   Critical Point

As would be expected, the glass compositions that exhibit high
critical temperatures are usually those that have higher softening
temperatures as shown in Table 2A. The difference between the
softening and critical point varies from 18 to 67°C and does not
appear to be composition dependent in any predictable fashion.

5.2.5   Coefficient of Thermal Expansion

Examination of the data on coefficient of thermal expansion shows
that substitution of sulfur for selenium or tellurium and substitution
of selenium for tellurium increases thermal expansion. These obser-
vations are in agreement with the respective expansion characteristics
of the separate elements. (As, 4.7; S, 64; Se, 37; Te, 16.8 x 10^{-6}/C^{o}).

41
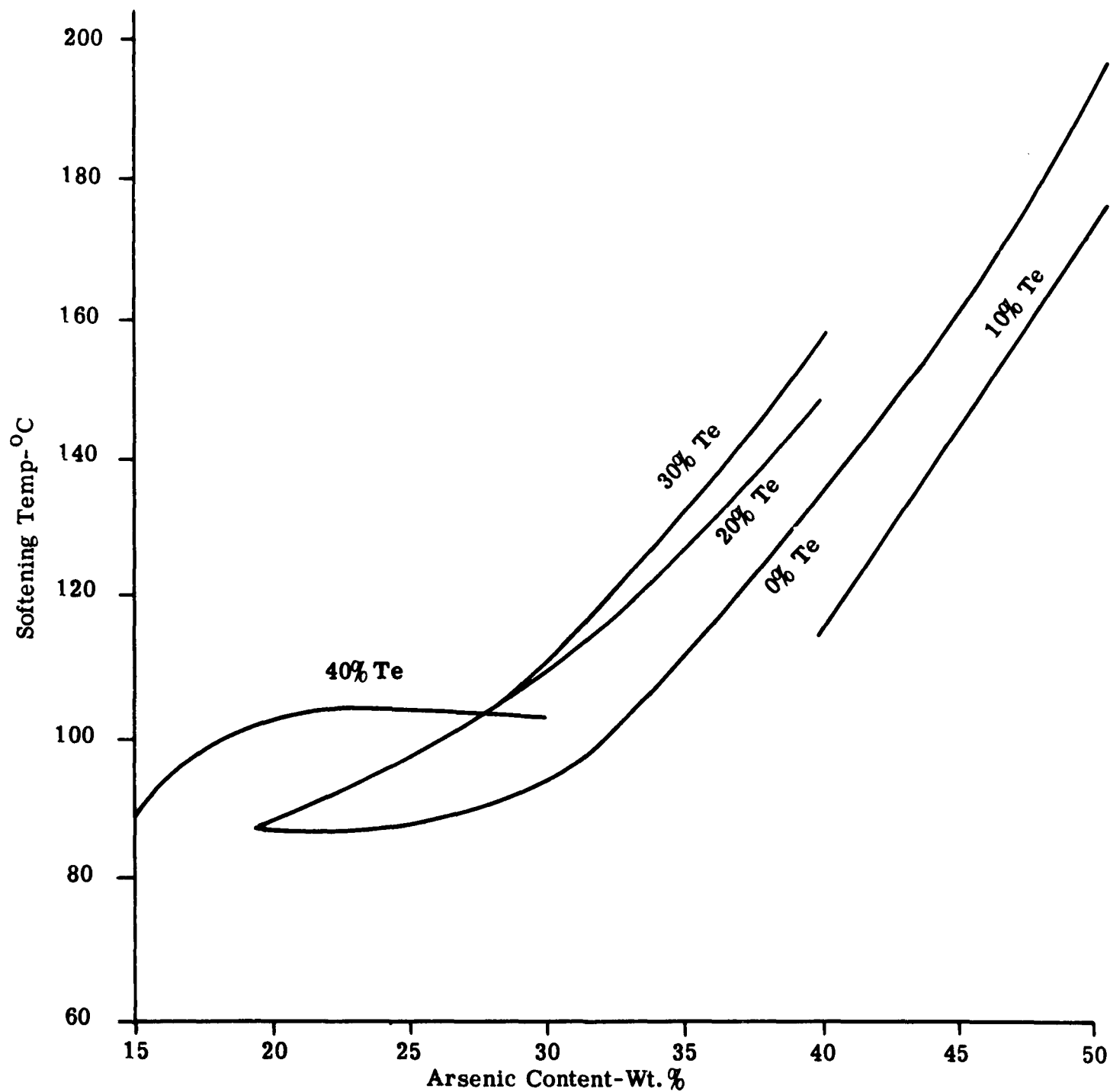
Figure 23. Softening Temperature vs. Arsenic
Keeping Tellurium Constant

5.3 Chemical Properties

All glasses exhibit good resistance to attack by water and dilute acids. Solubility in alkaline solutions, however, is appreciable and is a function of sulfur content of the glass and solvent concentration. It also varies directly according to the alkalinity of the reagent.

5.4 Electrical Properties

5.4.1 Resistivity

Resistivity is a function of composition especially with regard to S and Te content. Glasses high in S and low in Te (A-166, 63-145, 53-157) have higher resistivities than those having high Te and low S (A-215, 63-139, A-218). This was expected since S has much higher resistivity than Te.

5.4.2 Dielectric Constant

Those glasses which are the better dielectrics are usually those that are low in sulfur. This indicates that sulfur reduces the dielectric properties of chalcogenide glasses.

5.5 Mechanical Properties

5.5.1 The mechanical properties of brittle materials such as glasses are difficult to determine accurately, since the results obtained depend to a large extent on surface condition, sample temperature, and rate of loading.

These effects were minimized as much as possible in this program by careful attention to sample preparation and uniformity of test conditions and by averaging values obtained on a number of specimens of each composition.

5.5.2 Specific Gravity

The specific gravity of the 20 glasses is a linear function of sulfur content. The glasses containing 5% sulfur are highest and those with 40% sulfur are the lowest in specific gravity.

The relationship between specific gravity and refractive index is indicated in section 5.1.3 above.

5.5.3 Compressive Strength

The compressive strength values in Table 5 show considerable spread and it is felt that the manner of testing was largely responsible. The values were generally higher for these glasses than those for As-Se-Te glasses previously measured under Nonr 3647(00). This is believed to be the result of improvements made in sample preparation for this program.

5.5.4 Tensile Strength

Tensile strength apparently increases with As content.

The special care taken in preparation of the samples would account for the twofold increase in the mean tensile strength value over that measured in the previous program for As-Se-Te glasses.

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5.5.5 Hardness

Hardness is decreased by the substitution of sulfur for any other constituent. Conversely, an increase in hardness results when arsenic replaced S, Se or Te.

5.5.6 Young's Modulus

Values of Young's Modulus were reproducible within 8% for the three specimens measured for each composition. These values increased significantly with increased arsenic content.

5.5.7 Reworkability

All glasses except the three marked "P" in Table 2 showed good rework characteristics when slumped into blanks for refractive index prisms. Those glasses marked "P" however, could be satisfactorily cast from the initial melt and were considered suitable for inclusion in the group of 20 glasses measured.

6. Conclusions and Recommendations

6.1 With the completion of this program together with previous work done under Nonr 3647(00) the properties of a total of forty different glass compositions consisting of mixtures of two or more elements from the system As-S-Se-Te have been measured and evaluated. Selection of the glasses was based on criteria set up with the objective of making available for the design of high performance refractive IR

optical systems a group of materials suitable for most military and space applications. It can reasonably be stated that the initial exploration of the potential of this glass-forming system is complete.

6.2   Depending on composition, all 40 glasses transmit in the 2 to 5 and/or 8 to 14 micron atmospheric windows. They all soften above $100^{\circ}C$, and the range of refractive index and dispersion values represented is maximum for stable glasses in this system. Refractive indices range from 2.2 to 3.1 which, with the variety of dispersion characteristics available, indicates a high degree of usefulness for improved systems design. This is particularly true in the 2 to 5 μ range where achromatization is very difficult due to the higher order of dispersion in the shorter wavelengths for all optical materials.

In addition, the glasses can be fabricated into lens elements by essentially conventional optical shop techniques.

6.3   Although a number of these glasses have been melted satisfactorily in melts as large as two pounds, considerable work is needed to develop processing methods for the production of large melts. It is axiomatic in glass technology that melting procedures used to produce a glass in experimental quantities are not applicable to the production of larger batches. The differences in thermal masses require that heating and cooling cycles be modified accordingly.

These particular materials present additional problems in maintaining composition due to the range of vapor pressures at elevated temperatures among the constituents. Special provisions are required to prevent compositional changes due to loss by volatization of one or more of the components. If complete encapsulation is used to prevent this loss, practical methods of stirring and homogenizing must be developed.

6.4   As the most logical follow-up to this investigation, it is recommended that several refractive optical systems advancing the state-of-the-art be designed based on these glasses or on these glasses in combination with currently available materials. Formulation methods for appropriate quantities of the glasses applicable to the new designs should then be developed and prototypes of the systems fabricated and tested.

PART II

III - INVESTIGATION OF LONG WAVELENGTH INFRARED ABSORPTION

1. **General**

    1.1 Initial work on this part of the program was concentrated on the 12.8 micron absorption band which occurs in most glasses consisting of As-Se-Te.

    The possibility that this absorption is caused by residual impurities in the glasses was considered. Since very high purity raw materials (99.99+% or better) were used to formulate the glasses, the most likely offender seemed to be an oxide of one or more of the constituents. Two approaches were used in investigating this possibility — discrete additions of the oxides were made to controlled purity base glasses, and special techniques were used to eliminate oxides from the melts. As_2Se_3 and amorphous Se were used as base glasses since both can be prepared free of oxides by a simple distillation process and both are essentially free of absorption in the spectral region of interest.

    Measurement of infrared transmission spectra indicated that the above assumption is essentially correct, and that the original premise that this band occurs as a result of a subcrystalline arrangement within the structure of the materials was based on an incorrect assumption.

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1.2   An attempt was made to compare the absorption of the amorphous and crystalline forms of As_2Se_3, As_2Se_5 and As_2S_3 in order to determine the effects of the disorder of the amorphous structure on the fundamental absorption characteristics of the compounds. Efforts to obtain these compounds in crystalline forms were not successful. No definitive data, therefore, was obtained on this aspect of the absorption phenomena.

1.3   It was proposed that the compressibility of the chalcogenides under elevated temperature and pressure conditions and the resultant effects on such properties as index of refraction, density, and long wavelength absorption characteristics would provide additional insight into the basic structure of these materials. Accordingly, selected glasses were subjected to hydrostatic pressures up to 25,000 psi at temperatures slightly lower than their critical points, and the above properties were measured before and after the pressure-temperature experiments. Significant effects were found on refractive index and density, but no changes were noted in absorption characteristics.

2.   Investigation of 12.8μ Absorption Band - Experimental

   2.1   Base Glasses

     On the basis of our previous experience and that of others as reported in the literature, As_2Se_3 glass and amorphous Se can be processed to have sufficient stability and freedom from impurities so as to be essentially nonabsorbing to 14 microns.

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In each case, the base glass compositions were prepared by reacting high purity raw materials together in "Pyrex" tubes which had been evacuated and sealed under vacuum. After reaction, the materials were heated to above their boiling points at the low pressure and allowed to distill over a baffle which had been fabricated into the reaction tube. The pure materials condensed and were collected at the baffle as liquids where they solidified on cooling. Any oxides present condensed as solids outside the hot zone of the furnace, and refractory impurities remained behind in the distillation chamber. The purified raw materials were transferred to a dessicator after being immersed in an atmosphere of prepurified dry nitrogen, and a nitrogen atmosphere was maintained in the dessicator until the experimental glass batches were formulated. Specimens of the raw material melts were ground and polished, and the infrared transmission of each was measured from 2 to 15 microns. Transmission spectra of the base glasses are shown in Figures 24 and 25.

2.2   Oxide Additions

Oxides of As, Se and Te in amounts of 0.05 and 0.1% were added to each of the base glasses, and the batches were sealed under vacuum in "Pyrex" glass tubes of such length that the entire tube could be placed within the constant temperature zone of the melting furnace in order to prevent loss of the oxides from the melt by volatilization and
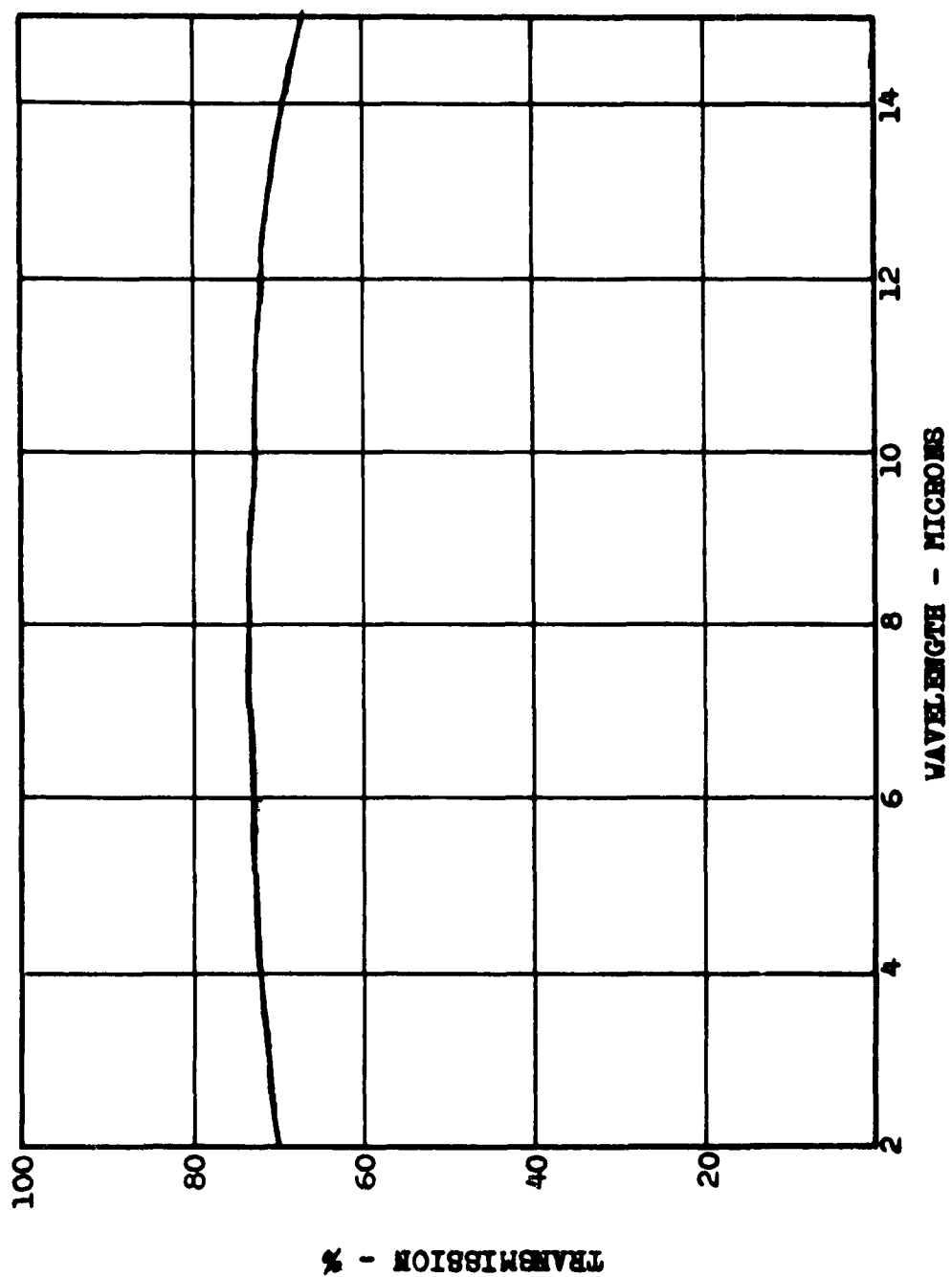
TRANSMISSION OF PURIFIED AMORPHOUS SELENIUM

Figure 24

TRANSMISSION OF PURIFIED As_2Se_3 GLASS

Figure 25

52
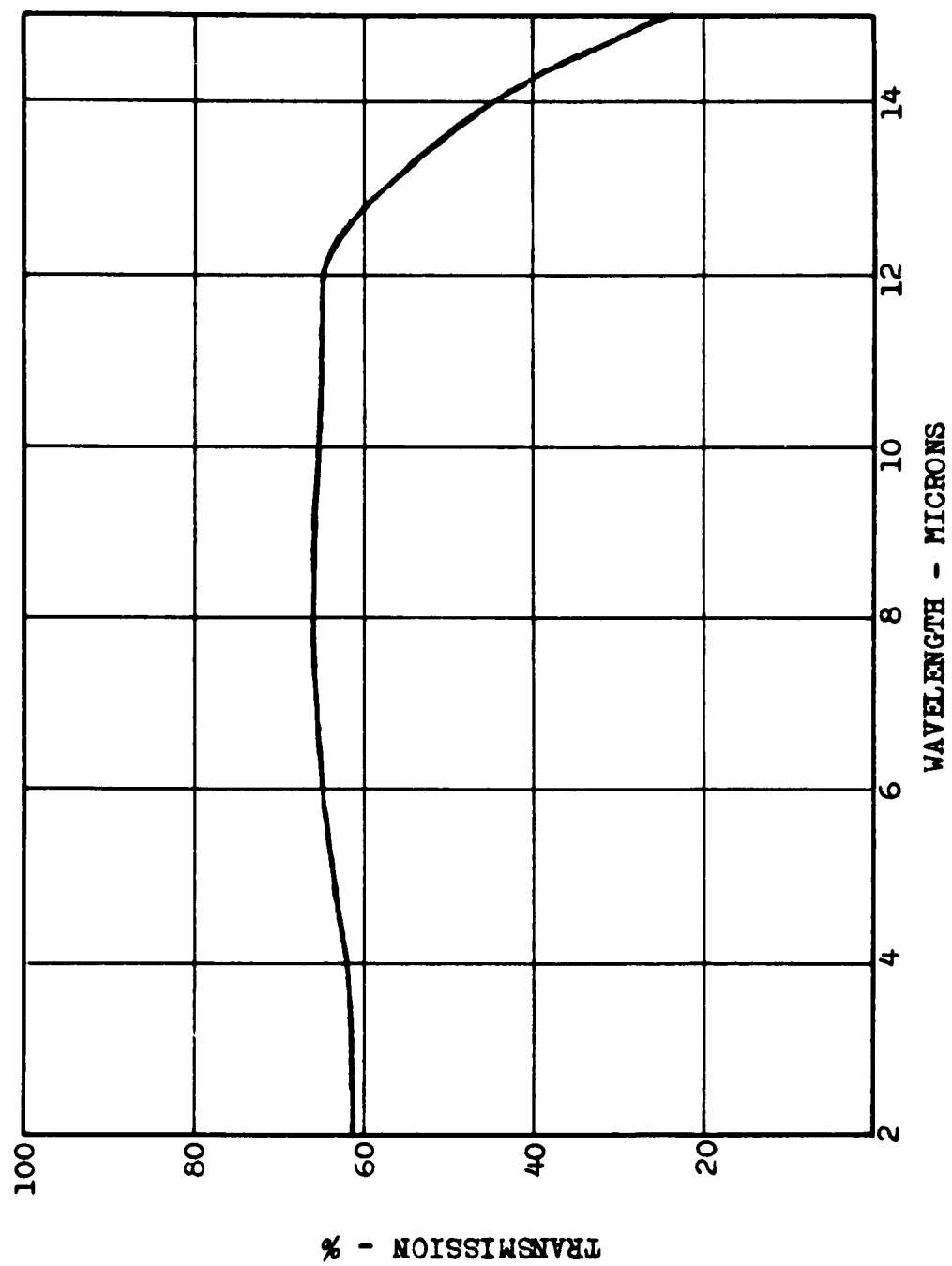
condensation. The melts were heated to 550°C and were thoroughly mixed over a period of 3 to 4 hours. The power was then turned off and the furnace allowed to cool to room temperature.

This proved a satisfactory procedure for the melts using As_2Se_3 as a base glass, but the selenium melts devitrified on cooling. In order to preclude this effect, subsequent selenium melts were transferred, after agitation, directly from the furnace at 550°C to another furnace which had been preheated to 70°C. They were allowed to remain at that temperature overnight, and the furnace was then turned off.

Specimens of the resultant glasses were ground and polished, and infrared transmission measurements were made from 2 to 15 microns. Figures 26 through 31 show results obtained from the oxide additions.

2.3 Transmission of Oxide Thin Films

In order to get an indication of the inherent absorption characteristics of the oxides themselves, thin films of As_2O_3, SeO_2 and TeO_2 were deposited on substrates of KRS-5 and NaCl by condensation from the vapor phase.

The oxides were prepared by passing oxygen gas over the heated metals in a long Pyrex tube. These were then placed in a test tube, the substrate specimen was placed over the mouth of the tube, and a burner

53
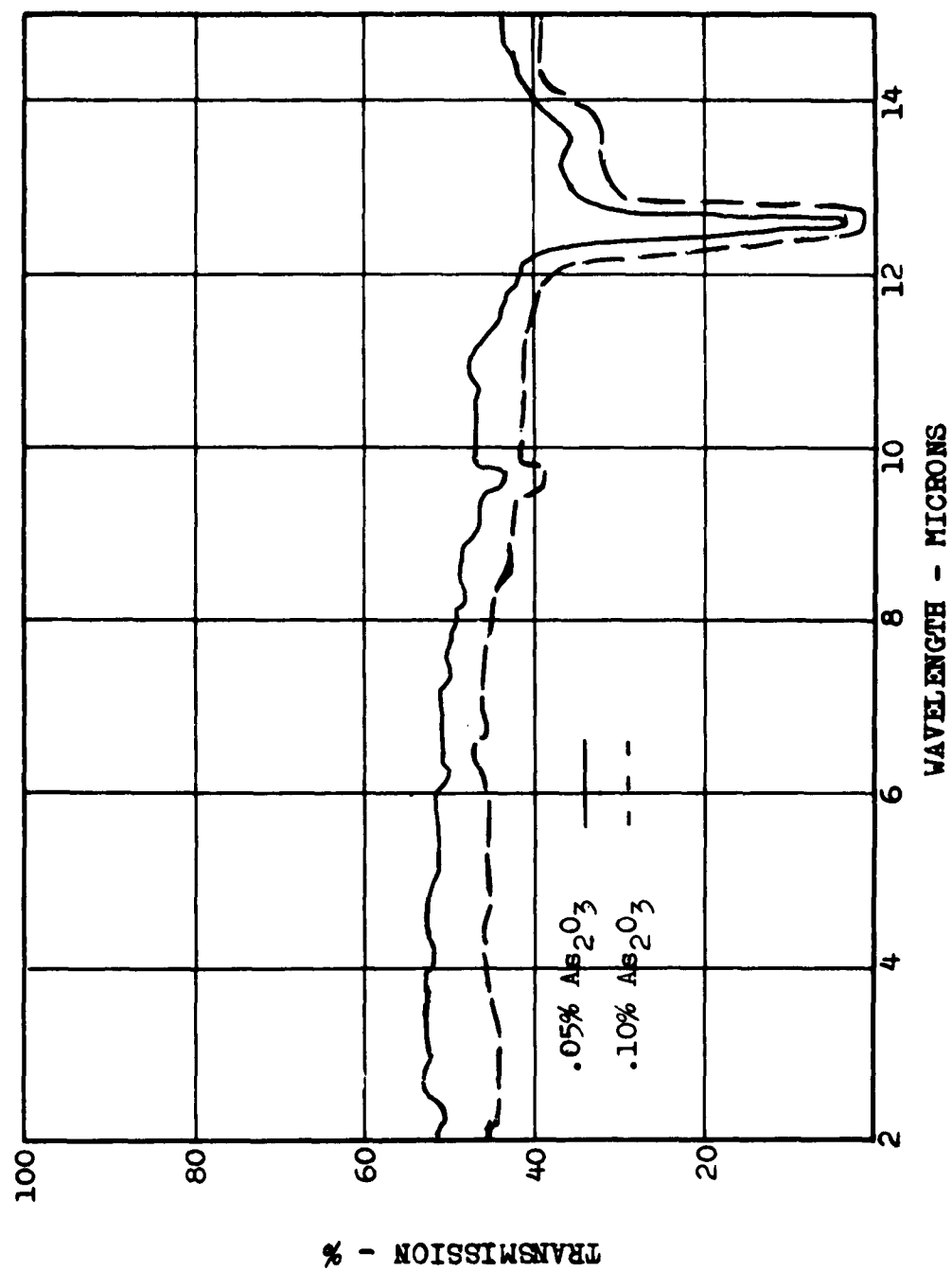
As$_2$O$_3$ ADDITIONS TO AMORPHOUS Se

Figure 26

54
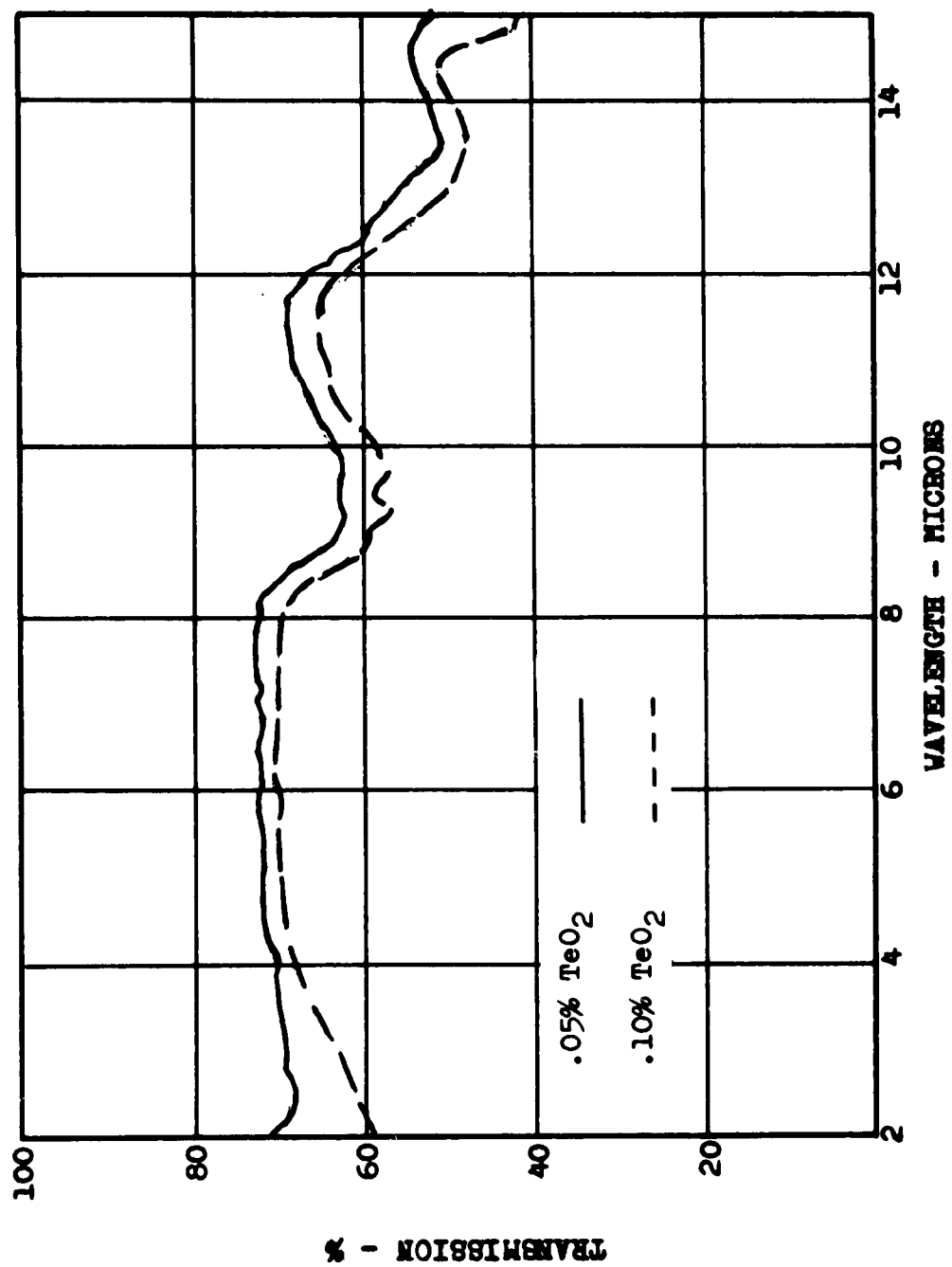
TeO$_2$ ADDITIONS TO AMORPHOUS Se

Figure 27

55
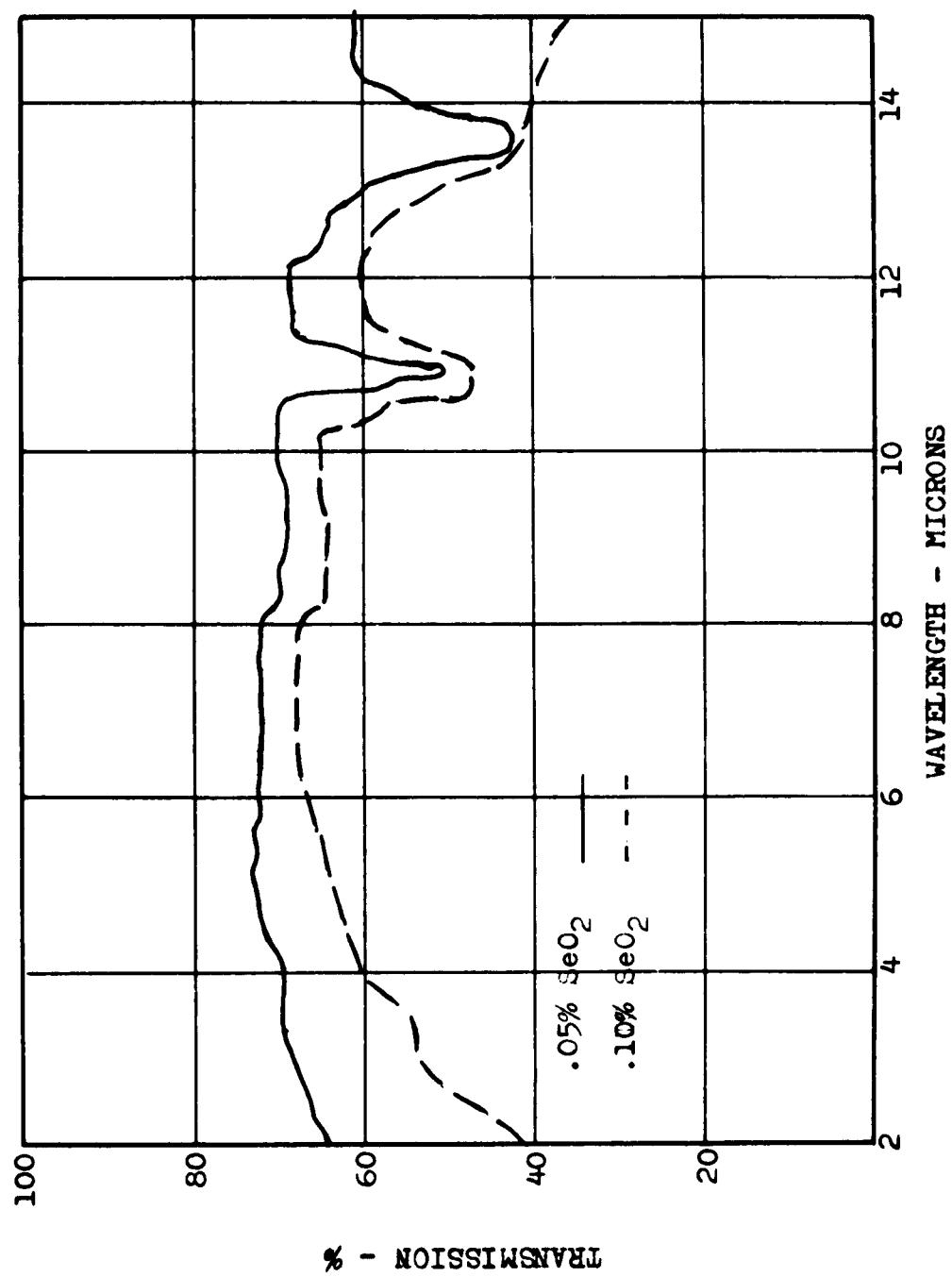
SeO$_2$ ADDITIONS TO AMORPHOUS Se
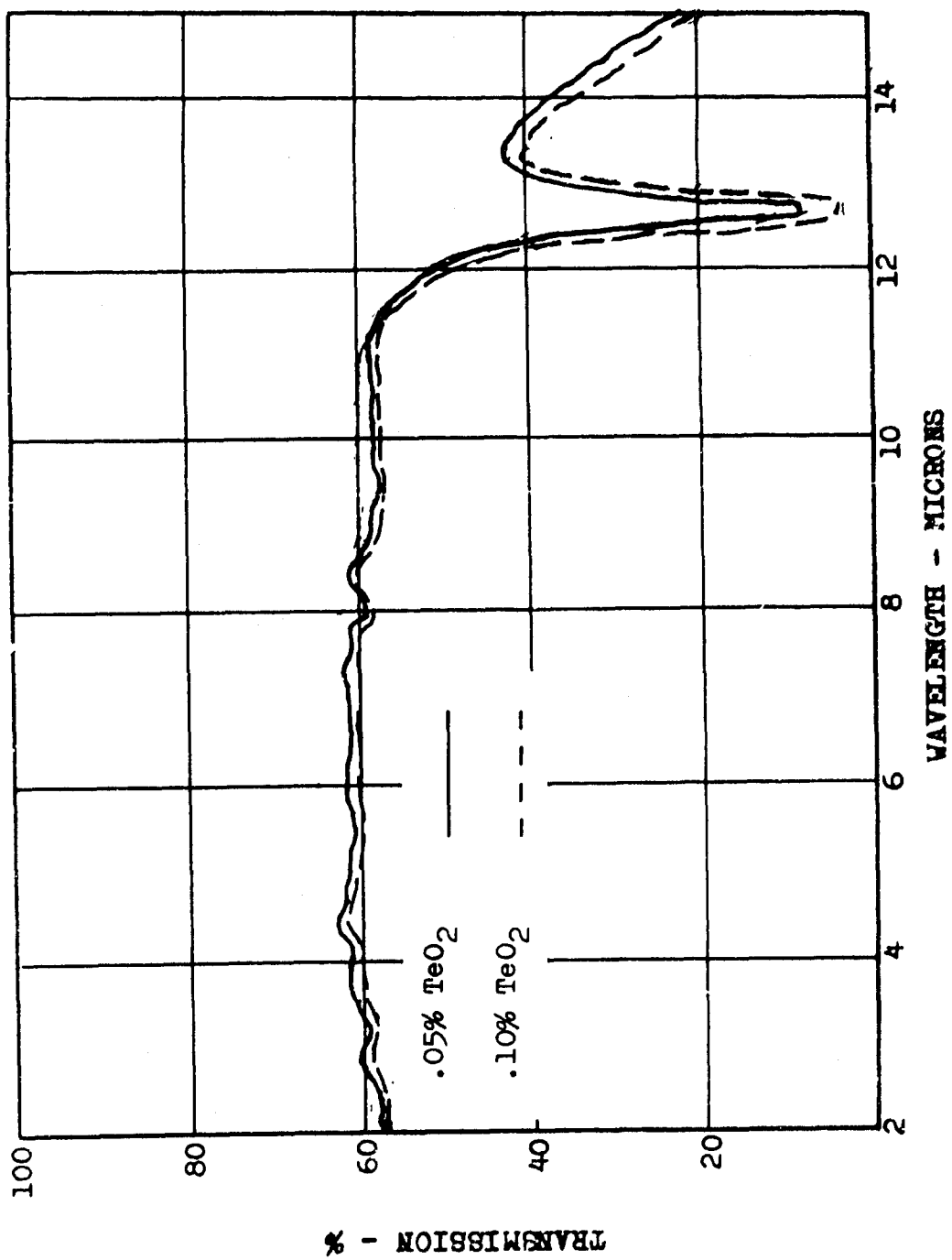
Figure 2.

TeO$_2$ ADDITIONS TO As$_2$Se$_3$ GLASS

Figure 29

57

WAVELENGTH - MICRONS
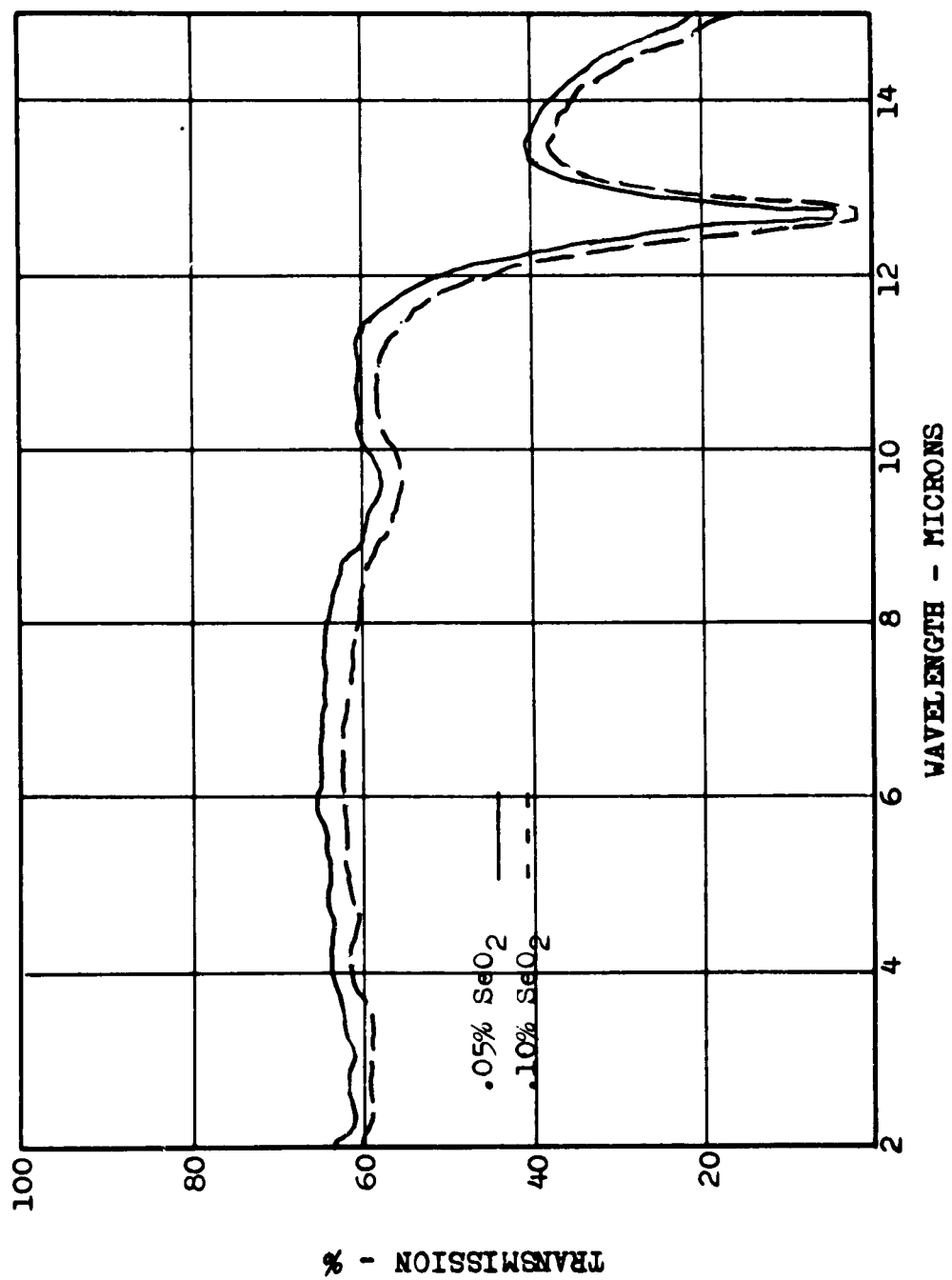
SeO_2 ADDITIONS TO As_2Se_3 GLASS

Figure 30
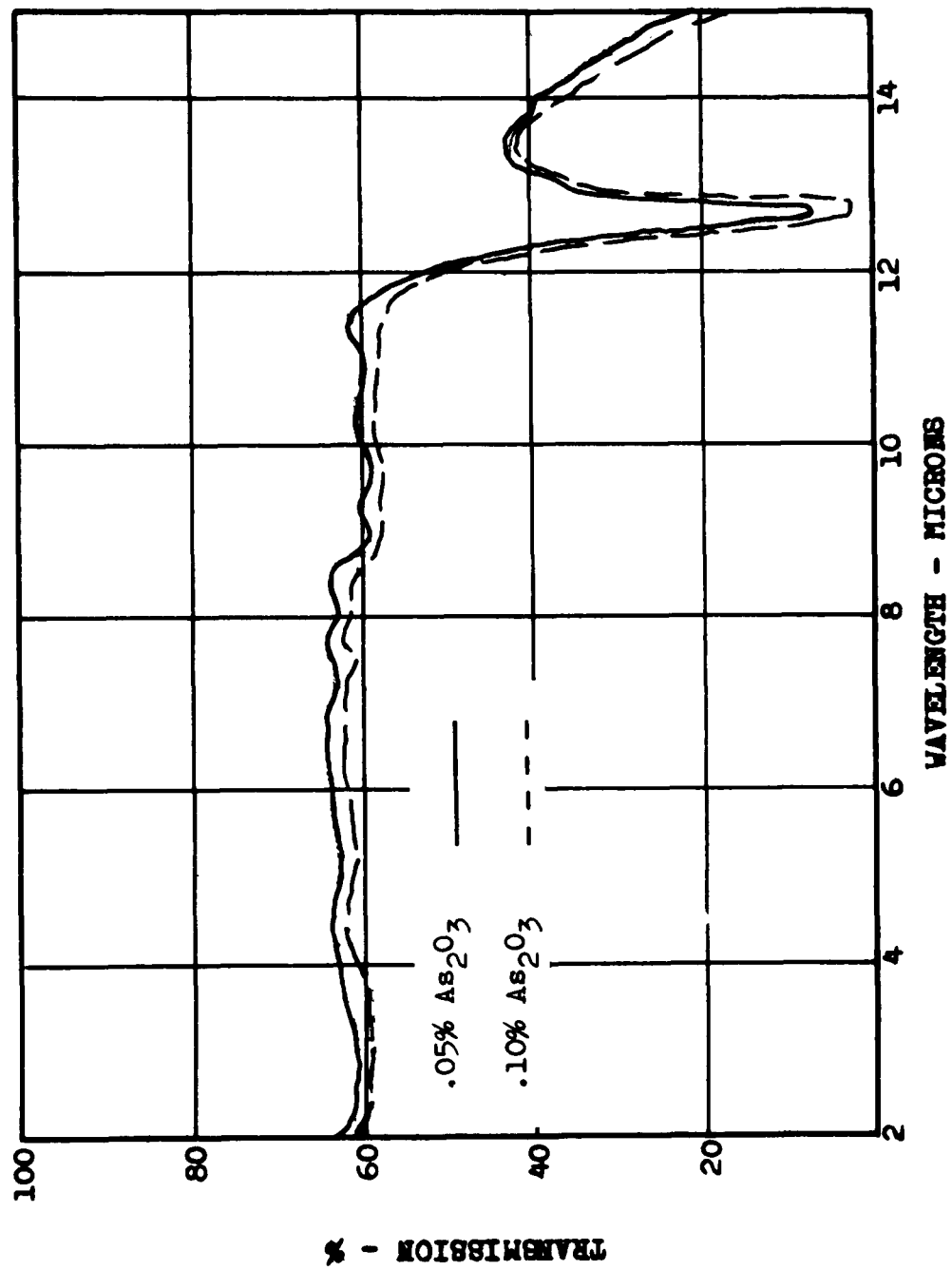
As$_2$O$_3$ ADDITIONS TO As$_2$Se$_3$ GLASS

Figure 31

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applied to the bottom of the tube until the oxide sublimed and an apparently even, uniform film collected on the substrate. No control of the film thickness was attempted other than to stop the process when visual observation indicated that the substrate was just completely covered.

KRS-5 was used as a substrate for As_2O_3 and TeO_2, but there was apparently a reaction between the condensing selenium oxide and the substrate so that no reliable transmission data could be obtained. Subsequent deposits of SeO_2 were made on polished plates of $NaCl$.

Figures 32, 33 and 34 show the transmission measurements obtained on the oxides of As, Se and Te.

2.4 Processing to Remove Oxides

Melts were made of the following compositions.

No.	As	Se	Te
62-73	38.7	61.3	--
62-74	27.5	72.5	--
62-76	40	25	35
62-77	30	30	40

Two batches of each composition were weighed out. One was encapsulated in a tube 6" long and the other in a tube 18" long. Both tubes were sealed after evacuation, and the long and short tubes of each composition were processed in the same furnace at the same time.

60
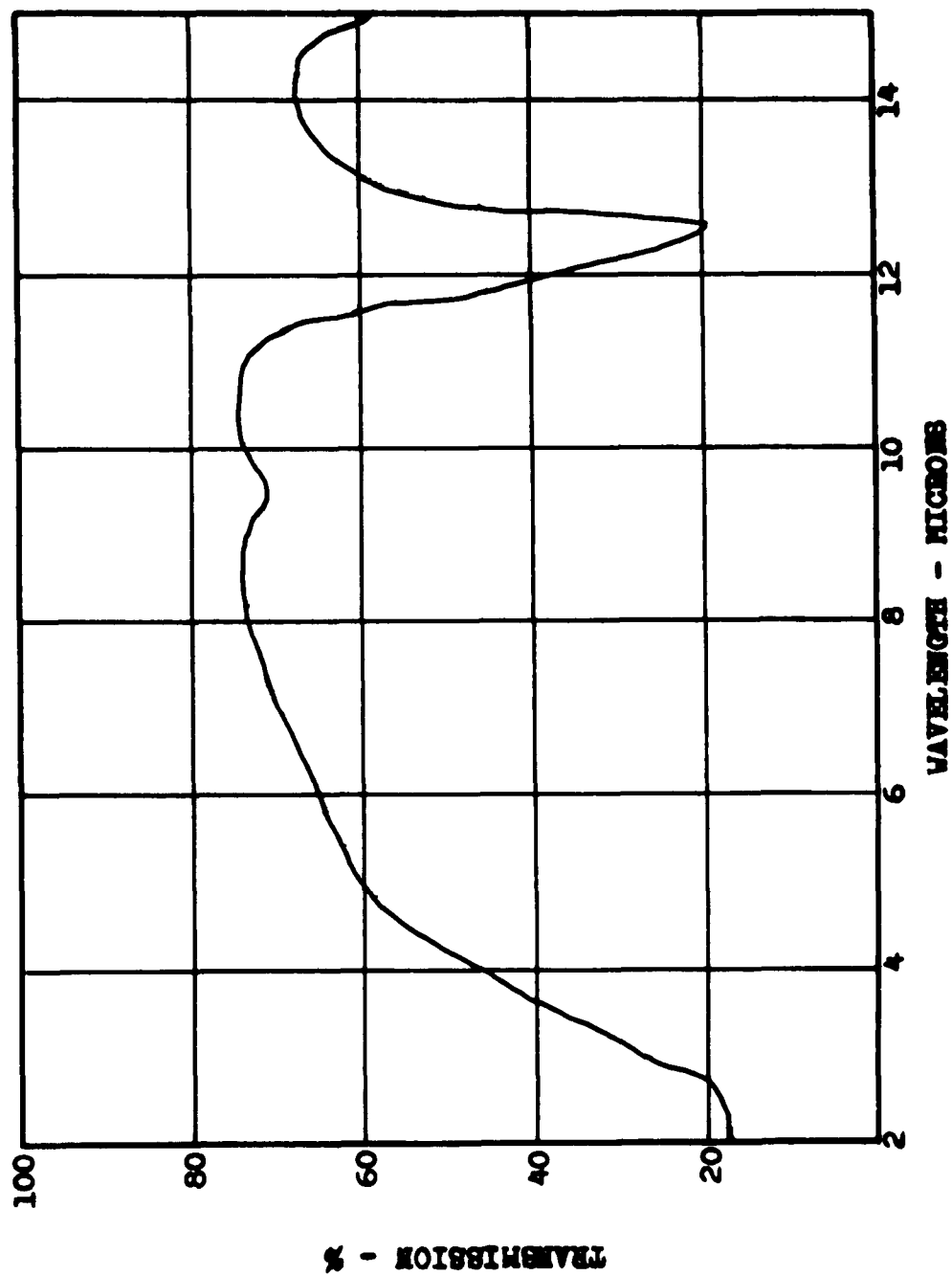
TRANSMISSION OF As_2O_3 THIN FILM ON KRS-5

Figure 32
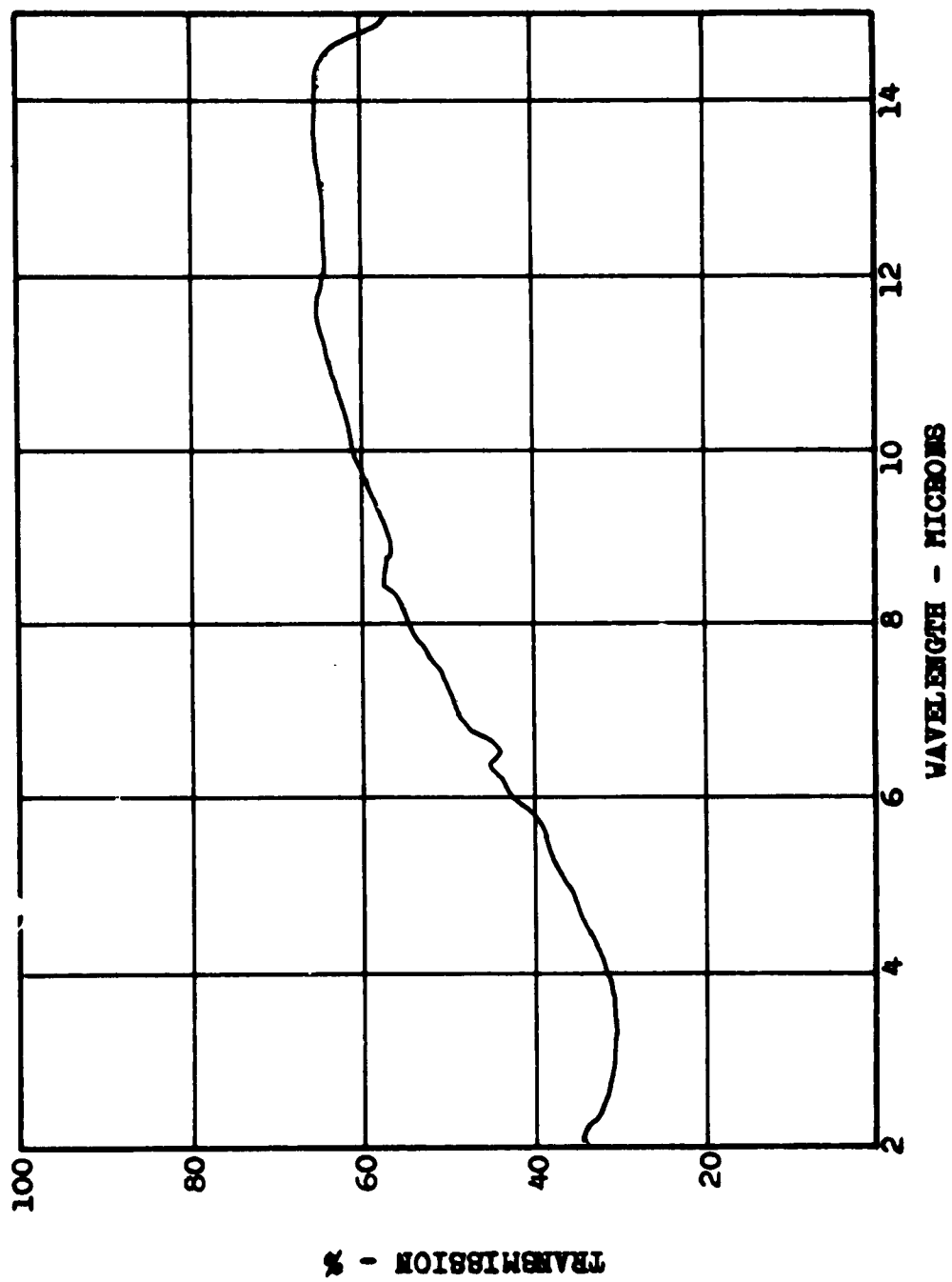
TRANSMISSION OF SeO_3 THIN FILM ON NaCl

Figure 33
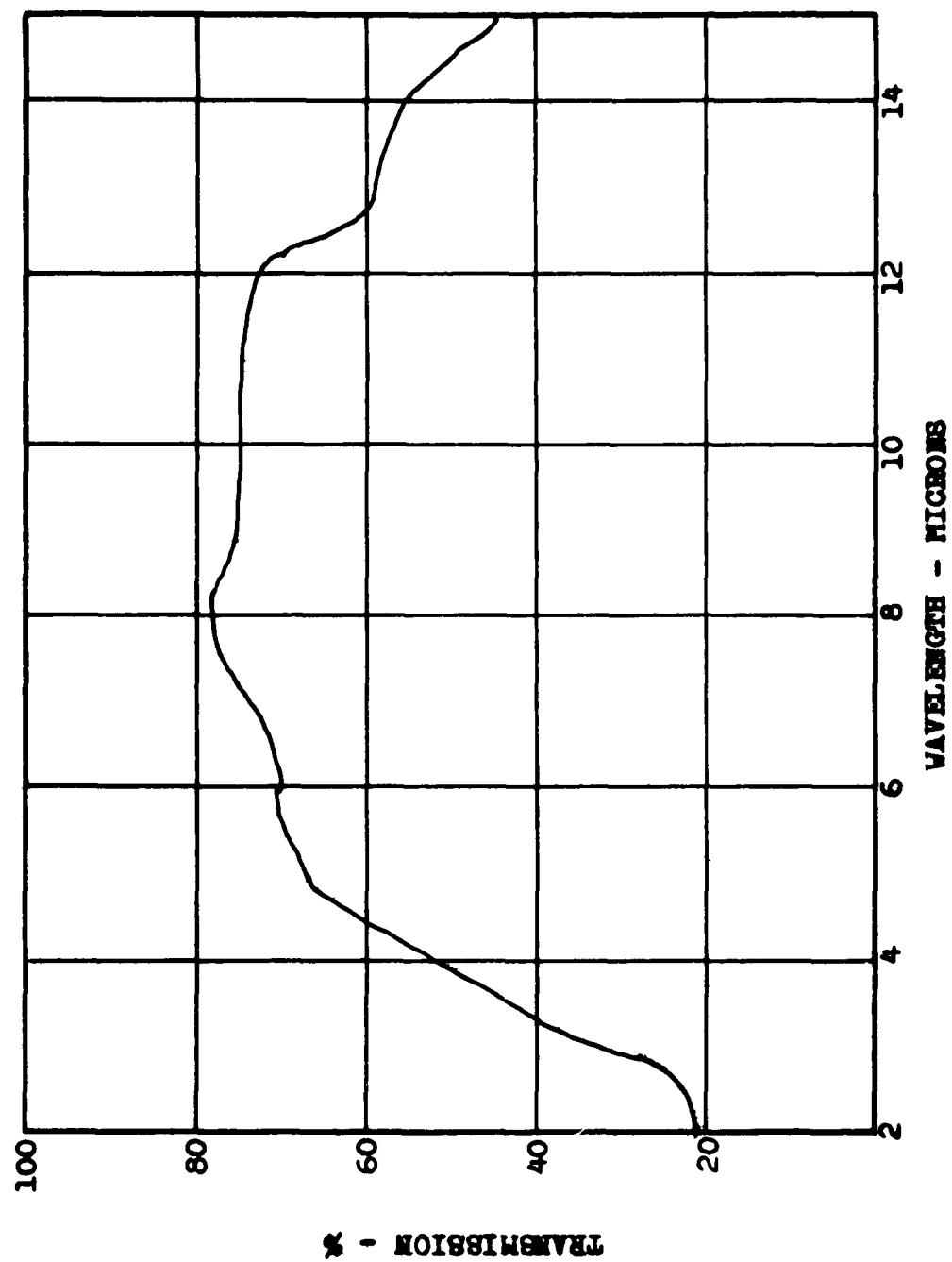
TRANSMISSION OF TeO_2 THIN FILM ON KRS-5

Figure 34

63

Both tubes were placed in the furnace so that their entire lengths were inside the zone of uniform temperature. The temperature was raised to $550^{\circ}C$ and maintained at that temperature for a minimum of four hours. The melts were homogenized by periodically removing the tubes from the furnace and shaking end-for-end. After the reaction was complete, the short tubes were left in the hot zone and the long tubes were raised and suspended so that the bottom end remained in the hot zone and the top end was at a temperature less than $190^{\circ}C$ — the temperature at which all oxides of the elements, As, Se and Te, would condense. They were allowed to stand overnight. The furnace was then turned off and the melts allowed to cool at furnace rate.

By this method, all oxides in the long tube melts were sublimed off and condensed at the cold end of the tube. Transmissions were measured on the two specimens (long and short tube) of each melt. See Figures 35 through 38.

64
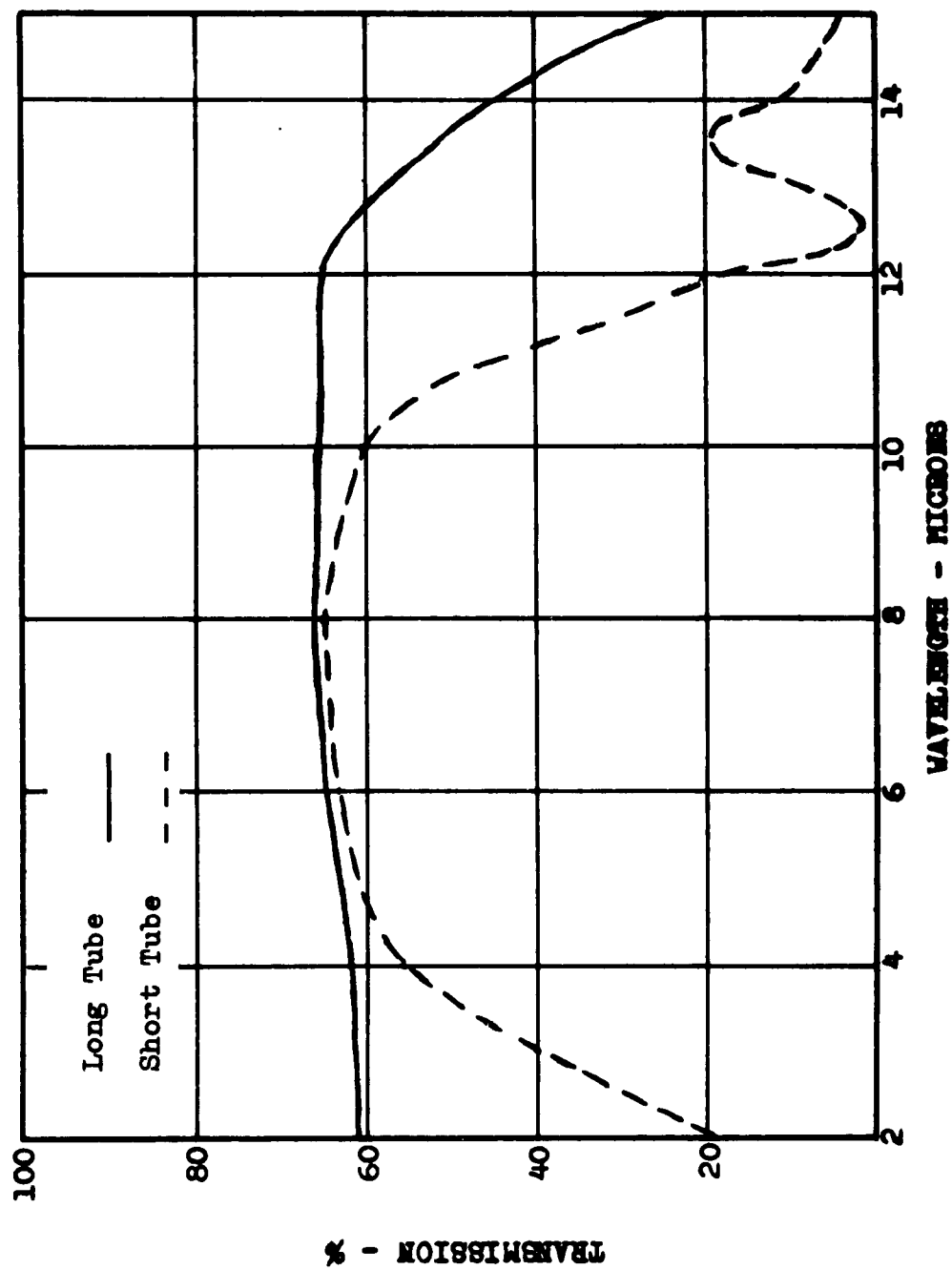
OXIDE REMOVAL - GLASS NO. 62-73

Figure 35

WAVELENGTH - MICRONS
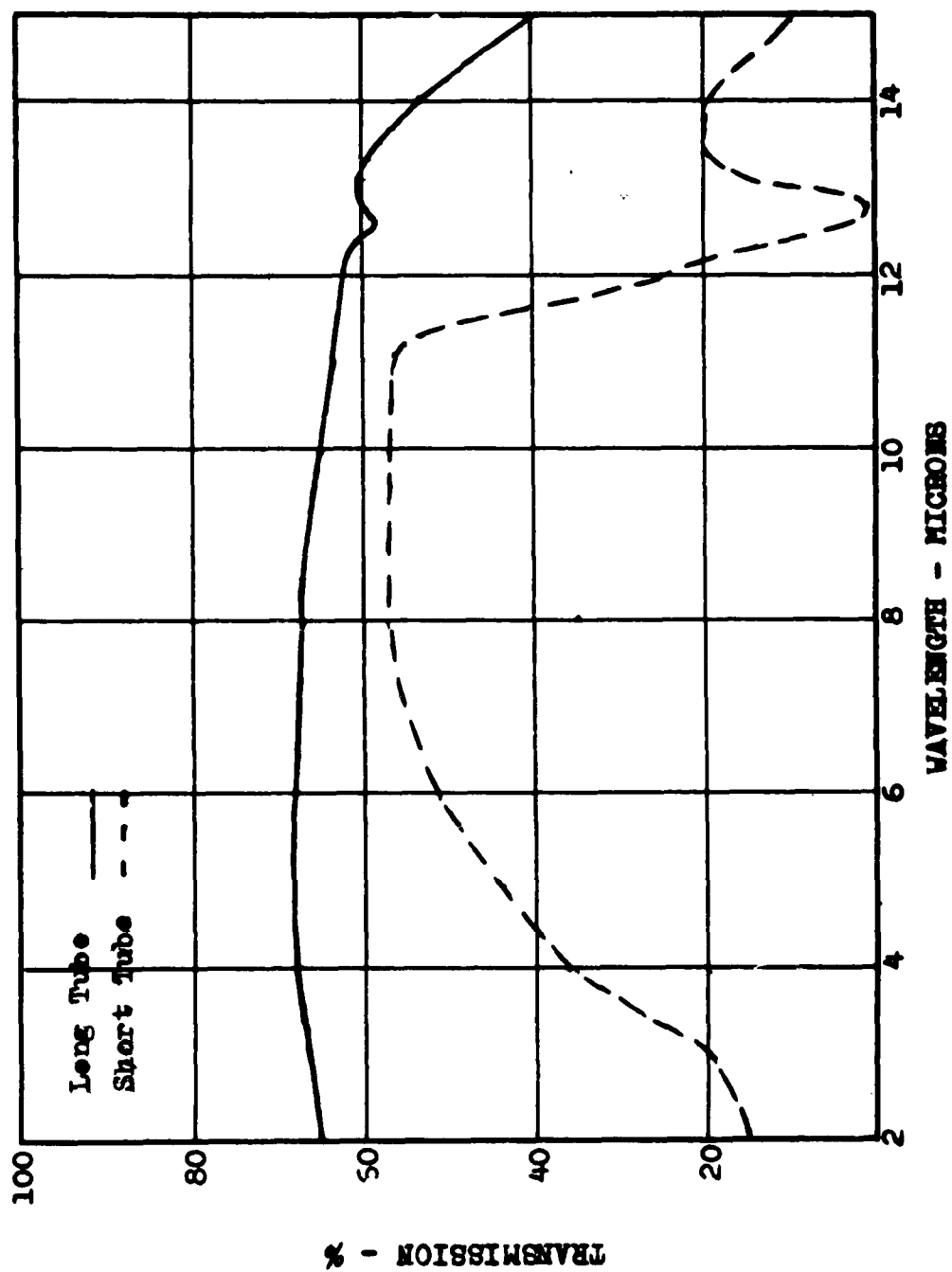
OXIDE REMOVAL - GLASS NO. 62-74

Figure 36
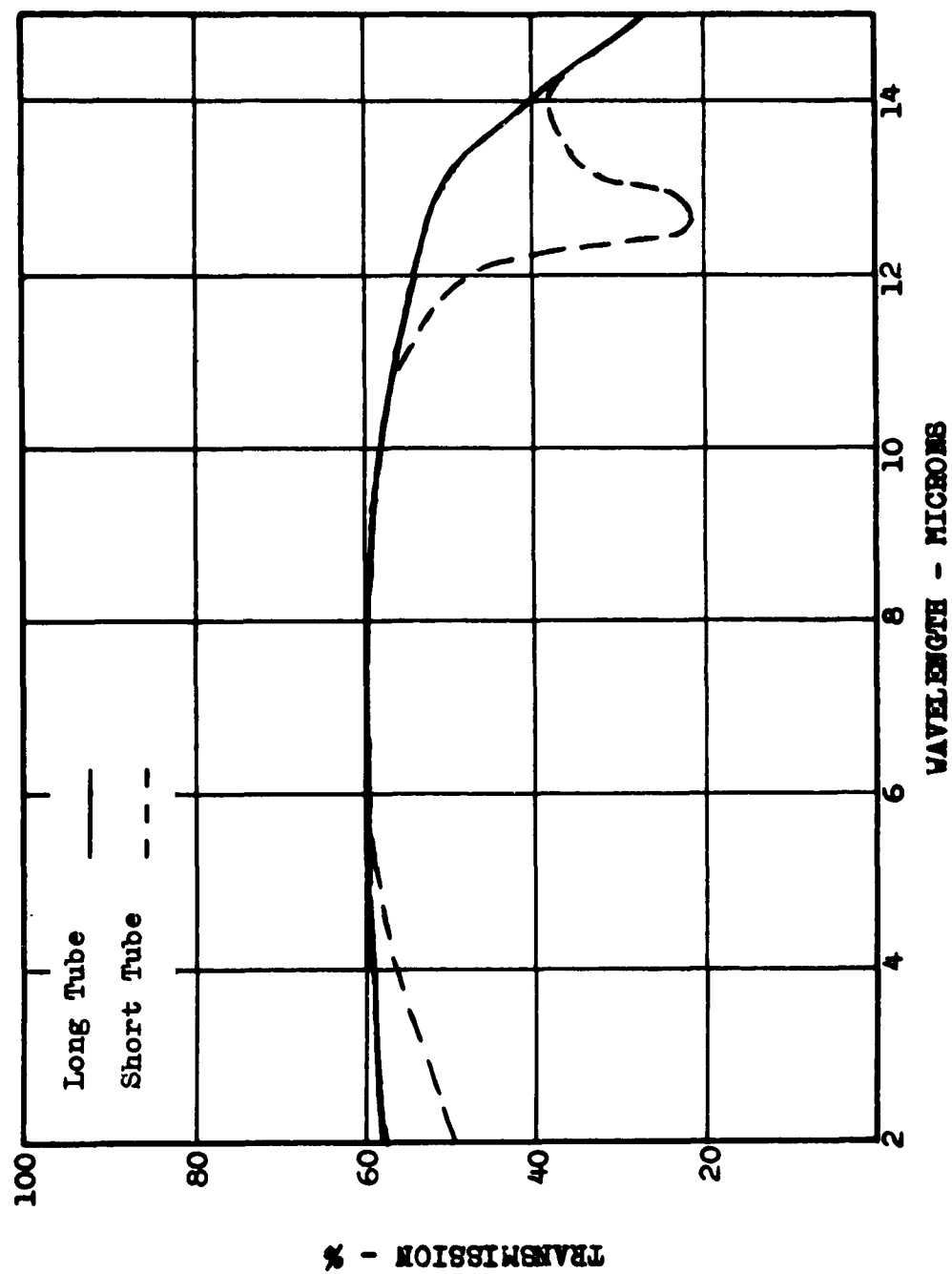
OXIDE REMOVAL - GLASS NO. 62-76

Figure 37

67

WAVELENGTH - MICRONS

TRANSMISSION - %
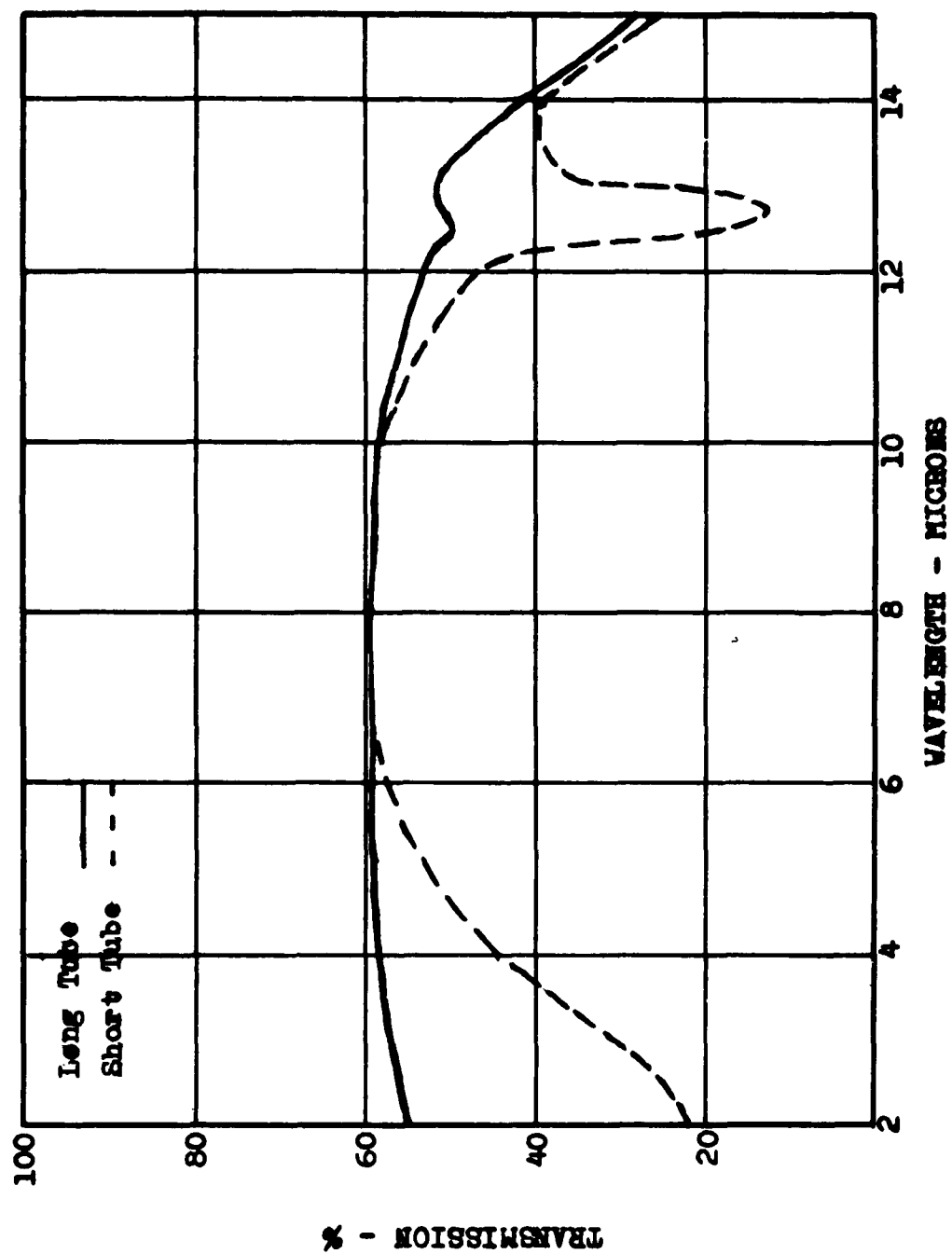
OXIDE REMOVAL - GLASS NO. 62-77

Figure 38

Long Tube

Short Tube

3.   Investigation of 12.8 μ Absorption Band — Results

3.1 No 12.8 micron absorption band was present in the base glasses.

3.2 Addition of oxides of As, Se and Te to As_2Se_3 produced the 12.8 micron absorption band to a degree proportional to the amount of oxide added.

3.3 Addition of As_2O_3 to Se produced the 12.8 micron absorption and an overall decrease of transmission. SeO_2 produced a band at 11 microns and a general decrease in transmission in the near infrared and at the longer wavelengths. TeO_2 produced some transmission reduction past 8 microns.

3.4 The transmission of the thin film of As_2O_3 showed strong absorption in the region between 12 and 13 microns. SeO_2 and TeO_2, on the other hand, showed no discrete absorption bands but rather a general decrease at the long and short wavelengths.

3.5 Processing of the glasses in long tubes so that the oxides are removed from the melt and condensed at the cold end of the tube eliminates or significantly reduces the 12.8 micron absorption band in all glasses tested. All glasses melted in short tubes so that the oxides were confined to the melt exhibited strong absorption at 12.8 microns.

4.   Investigation of 12.8 μ Absorption Band - Discussion of Results and Conclusions

4.1 It is apparent that oxide impurities are the cause of the absorption band at 12.8 microns. These originally could be oxides of any of the elements As, Se and Te.

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4.2   The facts that only As_2O_3 when added to amorphous selenium pro-
       duces specific absorption at 12.8 microns and that all the oxides
       produce this band when added to As_2Se_3 indicate that oxides of Se
       and Te react with As to produce As_2O_3 in the melt and the cations,
       Se and Te, are incorporated into the structure of the resultant
       glass.

4.3   Further indication that the specific cause of 12.8 micron band is
       As_2O_3 is provided by the transmission characteristics of thin films
       of As_2O_3, SeO_2 and TeO_2 in which only As_2O_3 exhibits absorption
       at this particular wavelength.

4.4   The above conclusions are strengthened by the fact that processing
       methods designed to remove oxides from the melt tend to eliminate
       or drastically reduce the absorption. Also, additional insight has
       been gained into practical methods of producing the glasses in suf-
       ficient quantity and quality for use in operational refractive systems.

5.   Comparison of Long Wavelength Absorption of Crystalline and Glassy
      Materials

5.1   The classical equation for the wavelength (λ) of absorption of radia-
       tion by an ion pair is:

$$\lambda = 2 \pi C \sqrt{\frac{\mu}{K}} \qquad \text{where} \quad \mu = \frac{M_1 M_2}{M_1 + M_2} \qquad (1)$$

       Here, μ is the reduced mass of the two atoms, C is the velocity of
       light and K is the force constant of the oscillator.

Assuming an inverse square law potential field between the two atoms

$$K = k \left[\frac{Z_1 Z_2}{R^2} \right] \qquad (2)$$

where Z_1 and Z_2 are the valences of the atoms, R is the ionic radius sum, and k is a proportionality factor. A useful approximation of the proportionality factor may be obtained by averaging the known constants of a number of single crystal materials. It is possible, therefore, to calculate the wavelength of the primary absorption of any pair of elements which might be considered for use in an infrared transmitting material.

This absorption will be modified and expanded by the number of modes of vibrations, the presence of impurities and structural defects.

5.2 Inherent in the vitreous structure is a high degree of disorder. It would be helpful, therefore, in the search for new infrared transmitting glasses to know something of the effects of this disorder which might be expected on the placement and width of the calculated fundamental absorption band. For this reason, we attempted to compare the absorption characteristics of the compounds As_2S_3, As_2Se_3 and As_2Se_5 in their crystalline and vitreous forms.

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5.3 We were unable to obtain single crystal specimens of any of these compounds. Furthermore, a review of the literature and communication with experts in the crystal-growing field failed to provide information as to how single crystals might be made.

Vaipolin[+] stated that As_2Se_3 could be completely devitrified by heating at $200^{\circ}C$ (the approximate softening point) for 10 to 20 hours. We reasoned that a devitrified thin film of the material should provide a good absorption spectrum. Films 6 and 9 μ thick of As_2Se_3 and As_2Se_5 were evaporated onto polished salt plates and heated to $210^{\circ}C$ for 48 hours without apparent devitrification.

The lack of results were attributed to the pheonomenon observed by the same author that crystallization was retarded at specimen surfaces in contact with the walls of the container.

The glasses were then fabricated as polished specimens of thickness ranging from .010" to .015" and again subjected to the above heat treatment. Again, there was no evidence of devitrification. The IR transmission curves before and after were identical except that the 12.8 absorption band appeared after heating - apparently some surface oxidation had taken place.

+ Vaipolin, et al, Soviet Physics - Solid State, 5, No. 1, 186-90 (1963)

We can only suppose that the reason our glasses did not devitrify as did those reported by Vaipolin is that the Russian glasses may have contained a sufficient amount of impurities to act as crystalline nuclei. Ours, on the other hand, had been specially purified and contained essentially no impurities to act as nuclei for incipient crystallization.

Although no data was obtained on the absorption of crystalline As_2Se_3 and As_2Se_5, it is considered significant, that the very pure glasses could not be devitrified. This consideration might be applied to other glass systems in which compositions exist which have desirable optical properties, but tend to be unstable in the vitreous state.

6. Investigation of Elevated Temperature - Pressure Effects: Experimental

6.1 Figure 39 shows a schematic of equipment purchased from American Instrument Company which was used to subject glass specimens to elevated temperatures and pressures. This equipment compresses inert gas (prepurified nitrogen, in this case) from a commercial cylinder and delivers it to a pressure bomb having a volume of 31.5 cu. in. The bomb is contained in a heating jacket, and the capacity of the equipment is 30,000 psi at 500^OF. The operation of the compressor and heating jacket is automatically controlled to hold pressure and temperature at any preset value within the range of the equipment.

73
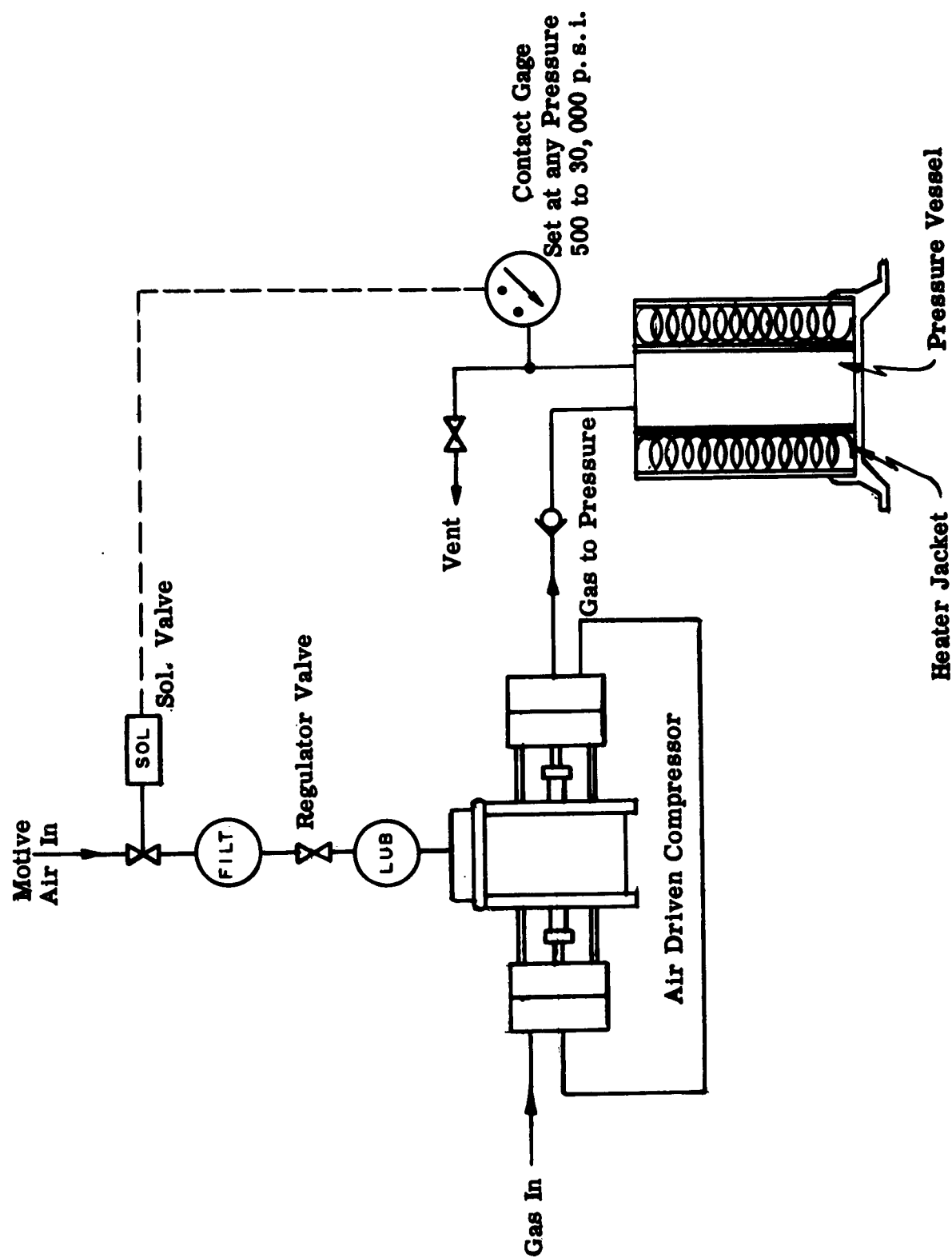
Figure 39. High Pressure - Temperature Equipment

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6.2 The glasses selected for these experiments were amorphous Se (discontinued), As_2S_3, As_2Se_3 and As_2Se_5. Three transmission samples 2, 4 and 6 mm thick, and an index of refraction prism was included in each series of pressure runs. Three series of pressure runs were made on each material. Two were made on glass purified by distillation and one on glass as-melted.

A limited series of experiments was also conducted on glasses containing As-Se-Ge for comparison purposes. The compositions of the As-Se-Ge glasses were:

Melt No.	As	Se	Ge	
63-16	20	50	30	% by Wt.
63-36	40	35	25	
63-40	5	65	30	

6.3 All specimens were annealed for 24 hours to stabilize, as much as possible, density and refractive index. Transmission samples and of the same materials were placed in the bomb and the bomb flushed with nitrogen. The pressure was raised to the required value, and the temperature was then increased to $10^{\circ}C$ below the critical point of the glass (As_2S_3 - $150^{\circ}C$, As_2Se_3 - $150^{\circ}C$, As_2Se_5 - $135^{\circ}C$). The samples were held at temperature and pressure for 4 hours and the heater was turned off and the bomb cooled to room temperature. The pressure was then released and the samples removed.

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Density, infrared transmission from 2 to 25μ, and refractive index from 2 to 10μ were measured before and after each run. Densities were measured on transmission samples.

In these experiments, pressure was the only variable - time and temperature being held constant. The pressures used for each series were 10000, 15000, 20000 and 25000 psi.

Work with amorphous selenium was discontinued after the 10,000 psi runs because all specimens fractured under that pressure.

6.4   The specimens of As-Se-Ge glasses were treated at 25,000 psi and $375^{\circ}C$ for 24 hours, and densities were measured before and after.

6.5   All specimens were then heated for 24 hours at atmospheric pressure and the same temperatures at which they were held under pressure. The densities were remeasured to determine the extent of residual compactness.

6.6   Data reported are averages of values for all specimens of any one material.

7.   Investigation of Elevated Temperature-Pressure Effects - Results

7.1   Transmission

Transmission characteristics from 2 to 25μ of the base glasses are shown in Figures 40 to 45.

76
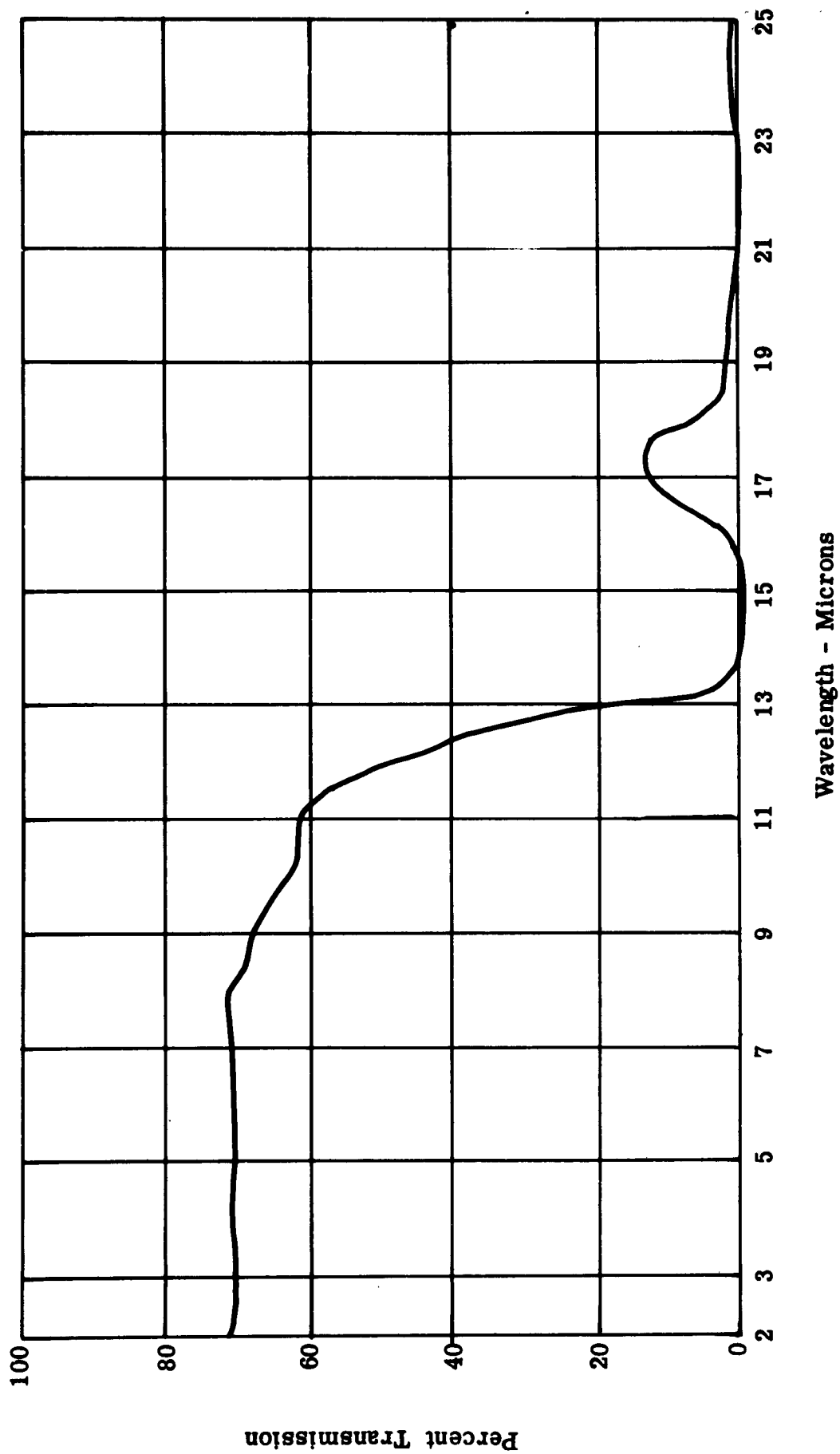
Figure 40. Transmission of As_2S_3 Base Glass
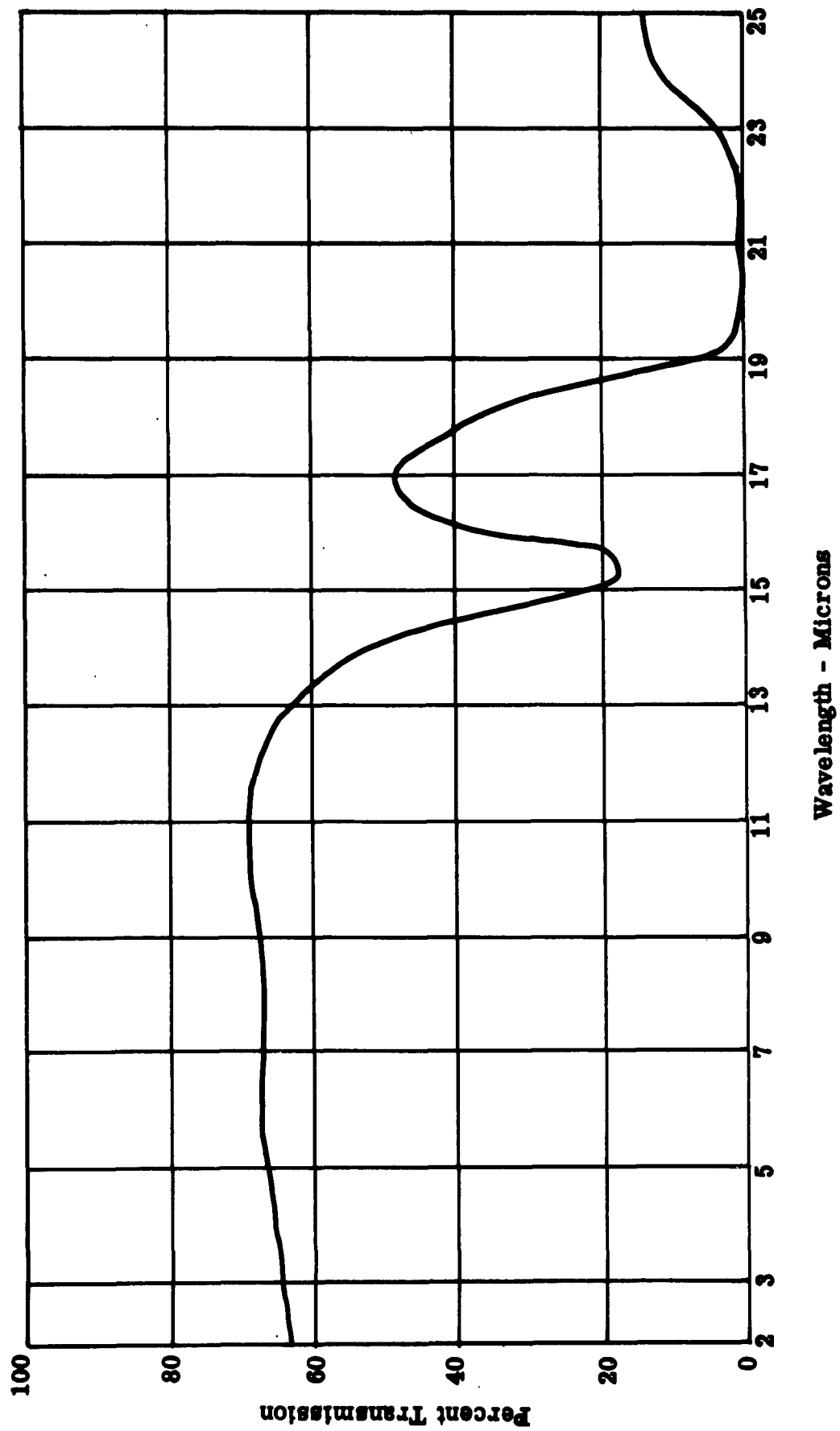
Figure 41. Transmission of As₂ Se₃ Base Glass

78
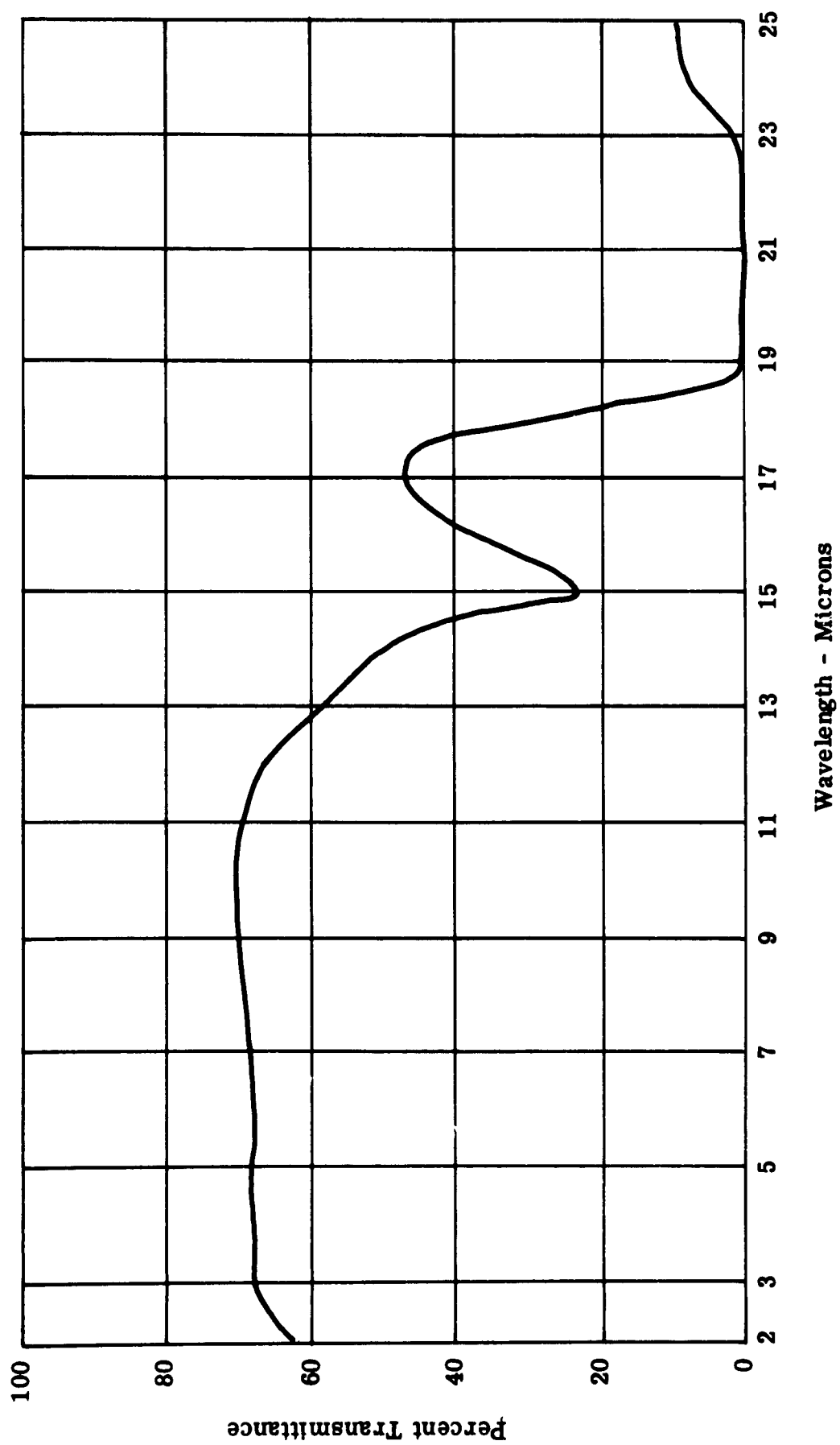
Figure 42. Transmission of $As_2 Se_5$ Base Glass
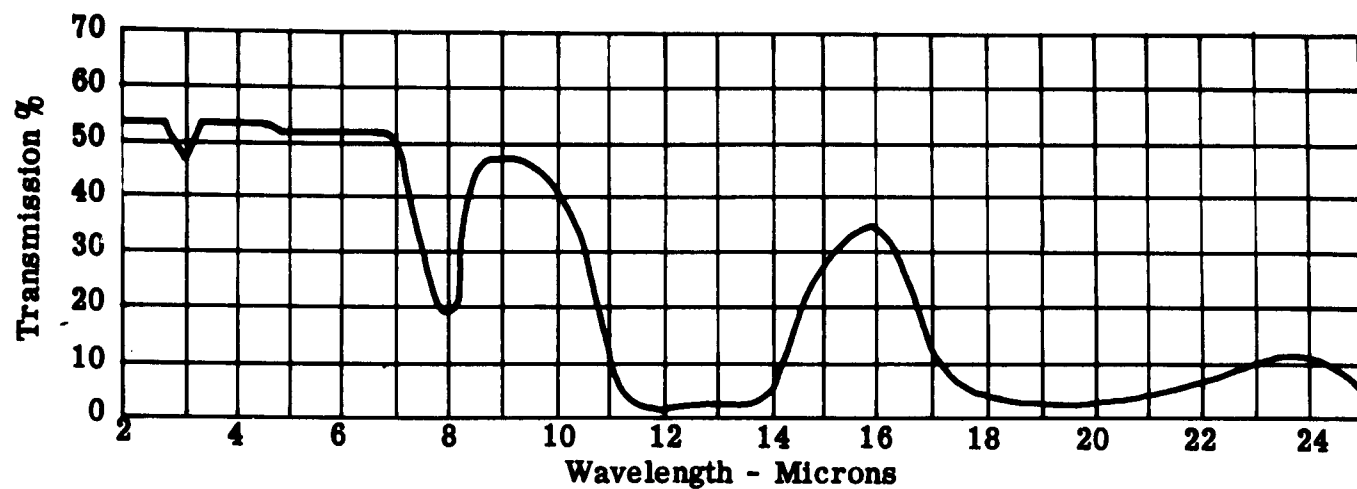
Figure 43.   Transmission of Glass No. 63-16
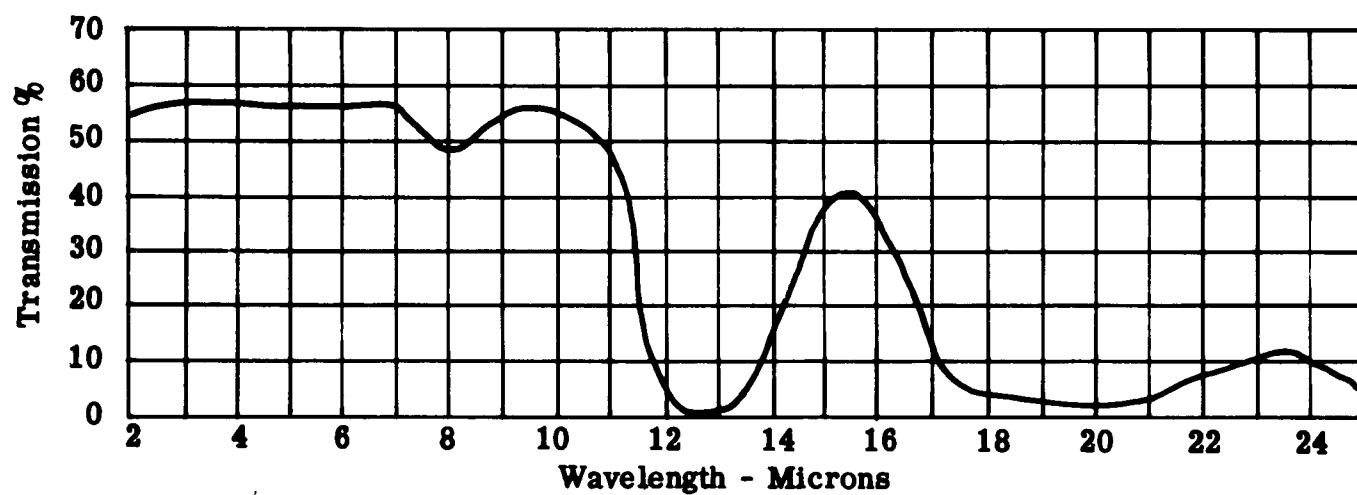
Figure 44.   Transmission of Glass No. 63-36
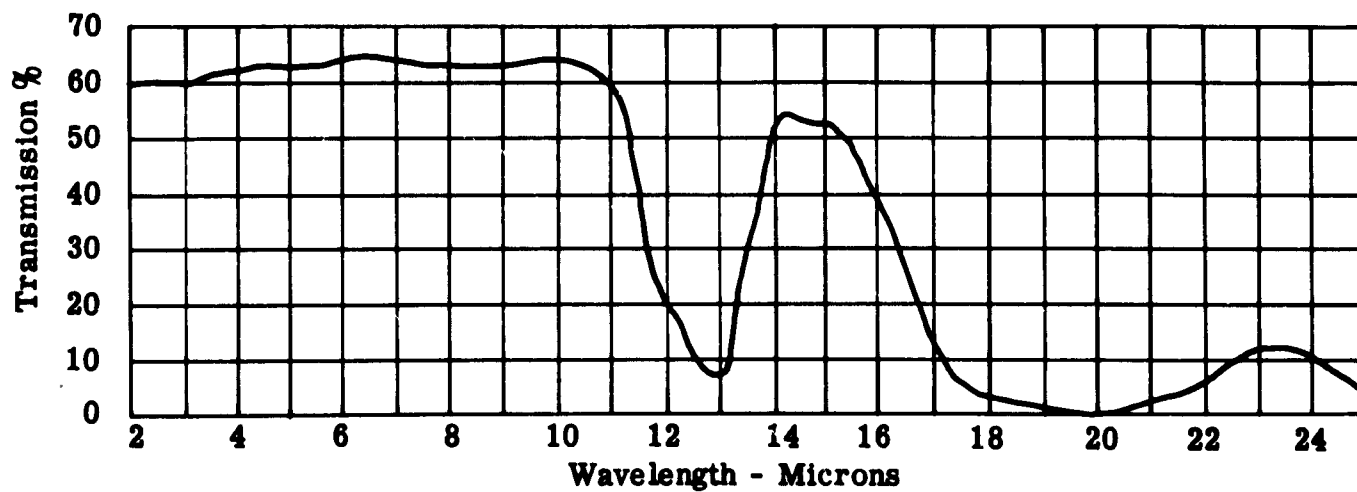
Figure 45.   Transmission of Glass No. 63-40

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There was no change in the transmission of any of the samples after being exposed to the high temperatures and pressures. This was true irrespective of the impurity level of the glasses as indicated by the 12.8μ absorption band.

The before and after transmission curves are identical, so no additional spectra are included in this report.

7.2 Density

The variations of density as a function of pressure for As_2S_3, As_2Se_3 and As_2Se_5 are shown in Figures 46, 47 and 48. Table 6 indicates the total change in density with 25,000 psi pressure for all samples and the residual density change after reheating at atmospheric pressure.

The changes in density with pressure of As_2S_3 and As_2Se_3 are essentially linear from atmospheric pressure up to 25,000 psi.

The density-pressure curve for As_2Se_5, on the other hand, shows a gradual decrease in slope as the pressure is increased.

The density increase of the germanium glasses was greater by a factor of 2 to 3 over that of the arsenic sulfide and selenides. The residual density increase after reheating was greater by an order of magnitude in the As-Se-Ge glasses.
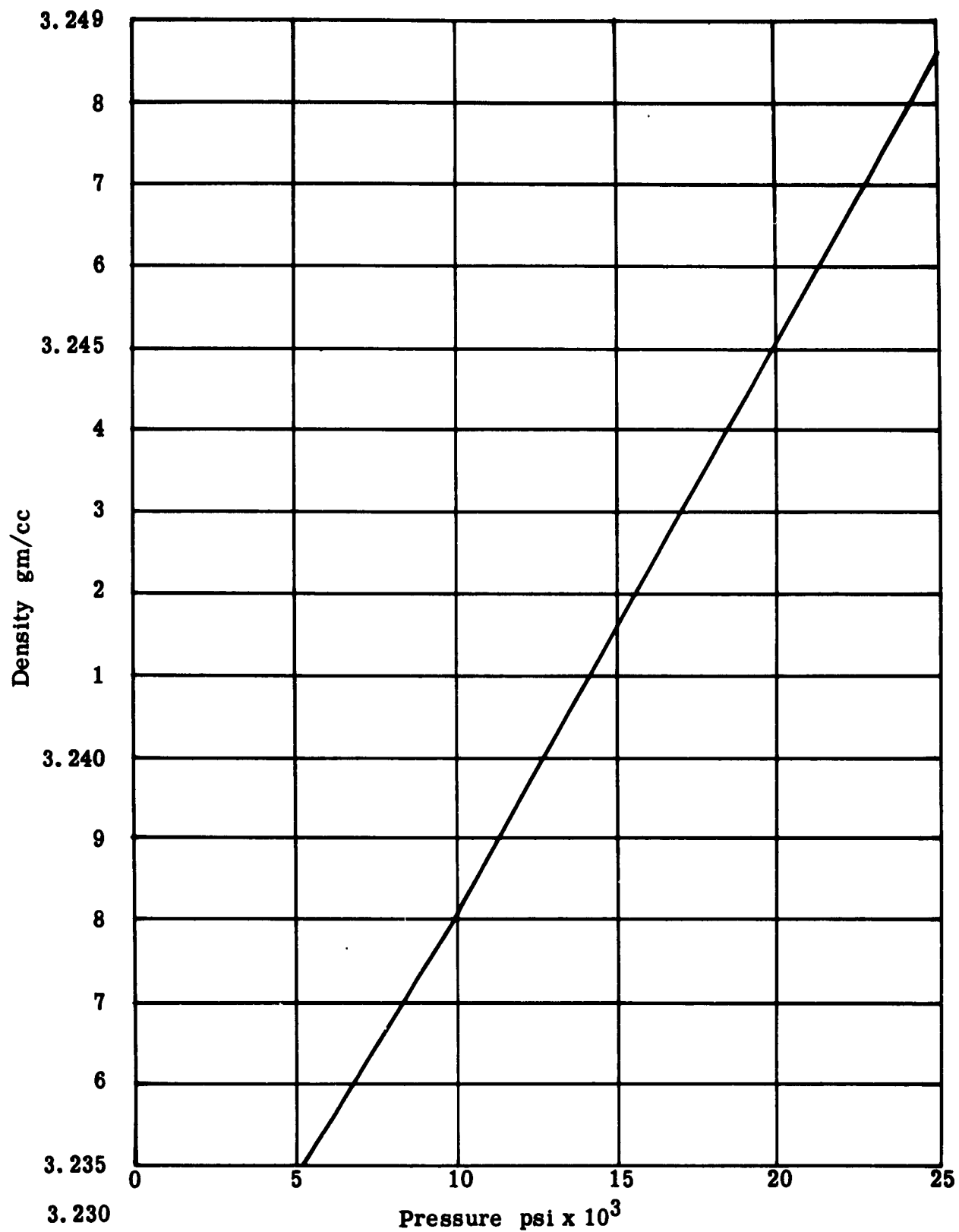
Figure 46.   Variation of Density with Pressure $As_2 S_3$ Glass
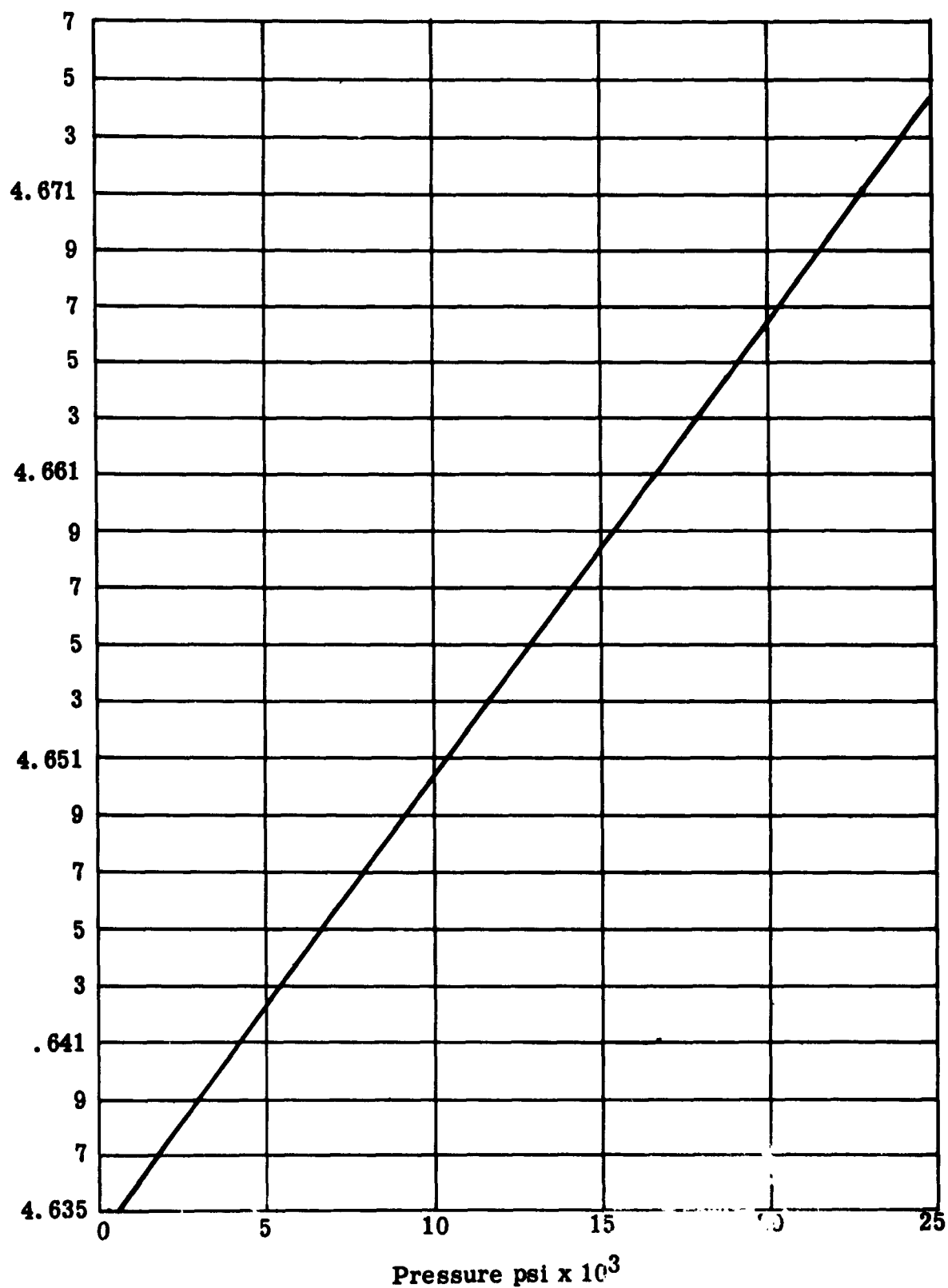
Figure 47. Variation of Density with Pressure $As_2 Se_3$ Glass

83
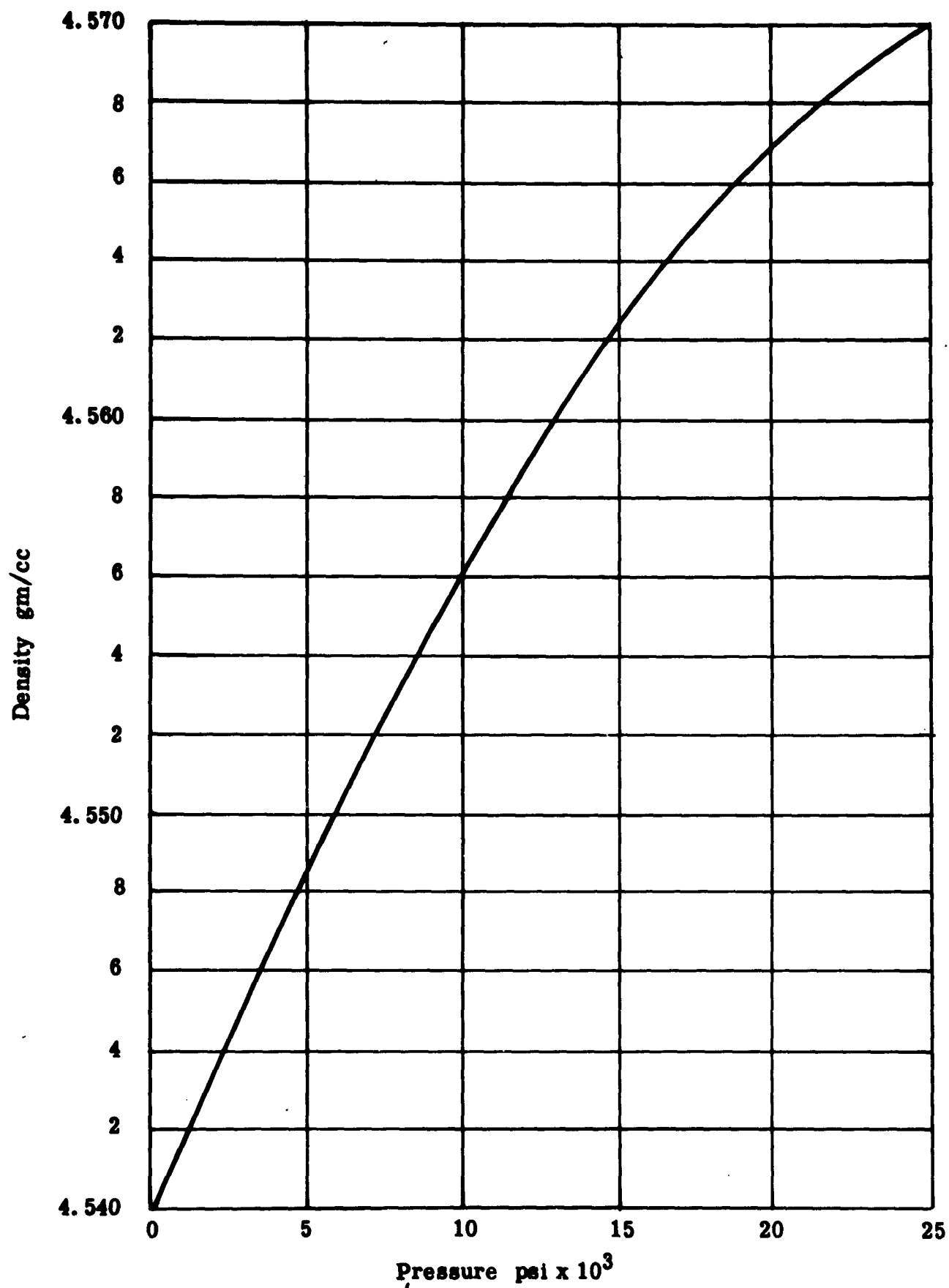
Figure 48.   Variation of Density with Pressure As$_2$Se$_5$ Glass

TABLE 6

DENSITY CHANGE AT 25,000 psi AND EFFECTS OF REHEATING

SPECIMEN	ORIGINAL DENSITY	DENSITY AFTER 25,000 psi	Δd	DENSITY AFTER REHEATING	RESIDUAL	Δd
As2S3	3.230	3.249	.019	3.242	.012	0.37%
As2Se3	4.633	4.671	.038	4.649	.016	0.35%
As2Se5	4.539	4.571	.032	4.543	.004	0.08%
As-Se-Ge Glasses						
64-16	4.496	4.564	.068	4.557	.061	1.36%
64-35	4.683	4.744	.061	4.733	.050	1.07%
64-40	4.340	4.404	.064	4.393	.053	1.22%

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7.3 Refractive Index

Figures 49, 50 and 51 show variations of refractive index of As$_2$S$_3$, As$_2$Se$_3$ and As$_2$Se$_5$ with pressure at discrete wavelengths, and Figures 52, 53 and 54 show index vs. wavelength values (dispersion) for each pressure level used in these experiments.

No index measurements were made on the As-Se-Ge Glasses.

8. Investigation of Elevated Temperature - Pressure Effects: Discussion of Results and Conclusions

8.1 Although significant compaction was noted in all specimens, there was no apparent change in infrared transmission to 25 microns. This would indicate that, while the general structure may have been modified as a result of pressure, the interatomic bonding between ion pairs within the structure was not disturbed sufficiently to change their normal vibrational frequencies to any appreciable extent. Also, there is no apparent change in the interatomic vibrational modes which would affect the side bands to the primary absorption.

In addition, there is no evidence of nucleation occurring within the structure - either of the base glasses themselves or of oxide im-purities - which would have been indicated by scattering of the short wavelengths. This would have caused a transmission decrease in the neighborhood of 2μ.

86
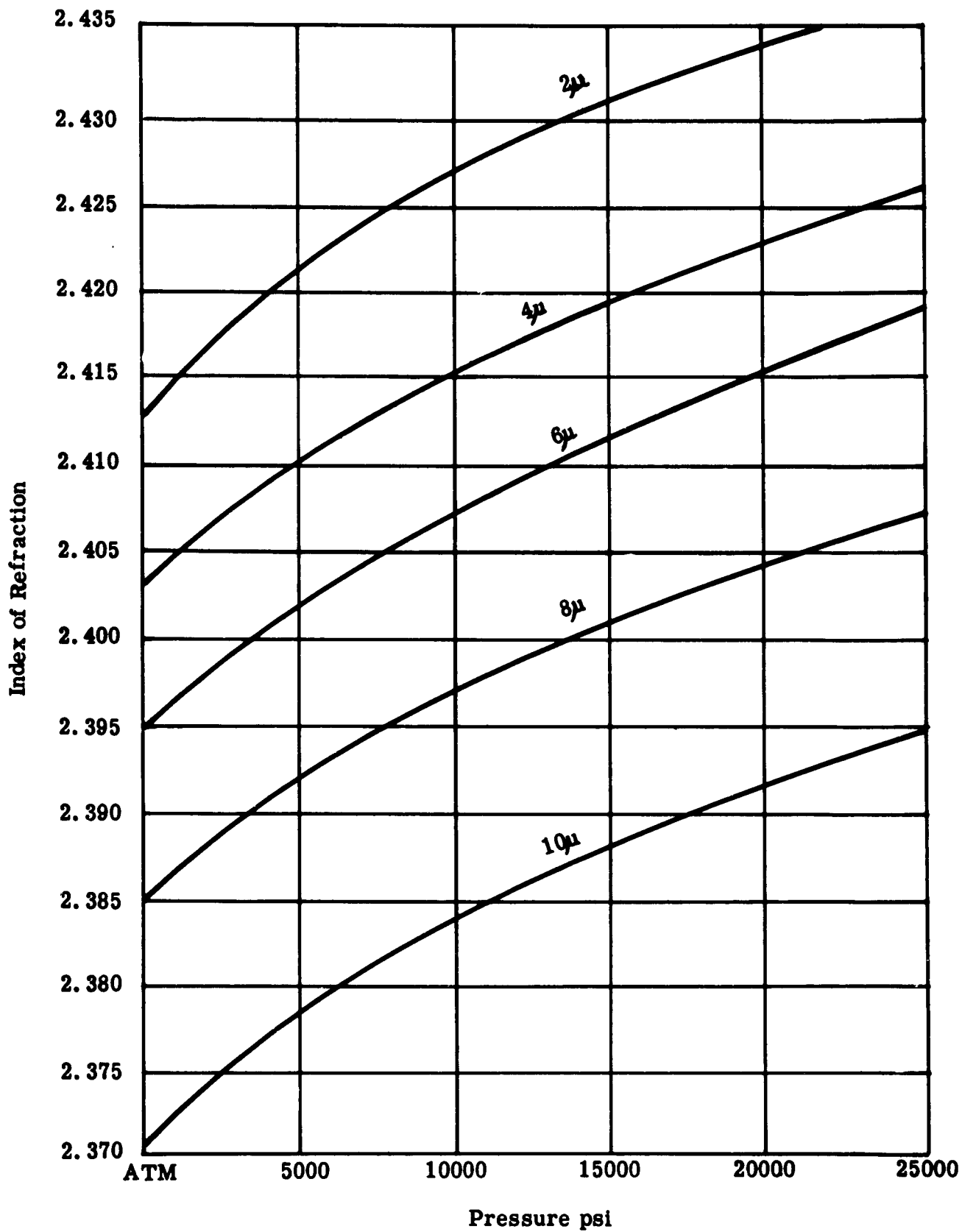
Figure 49. Variations of Refractive Index with Pressure As_2S_3 Glass
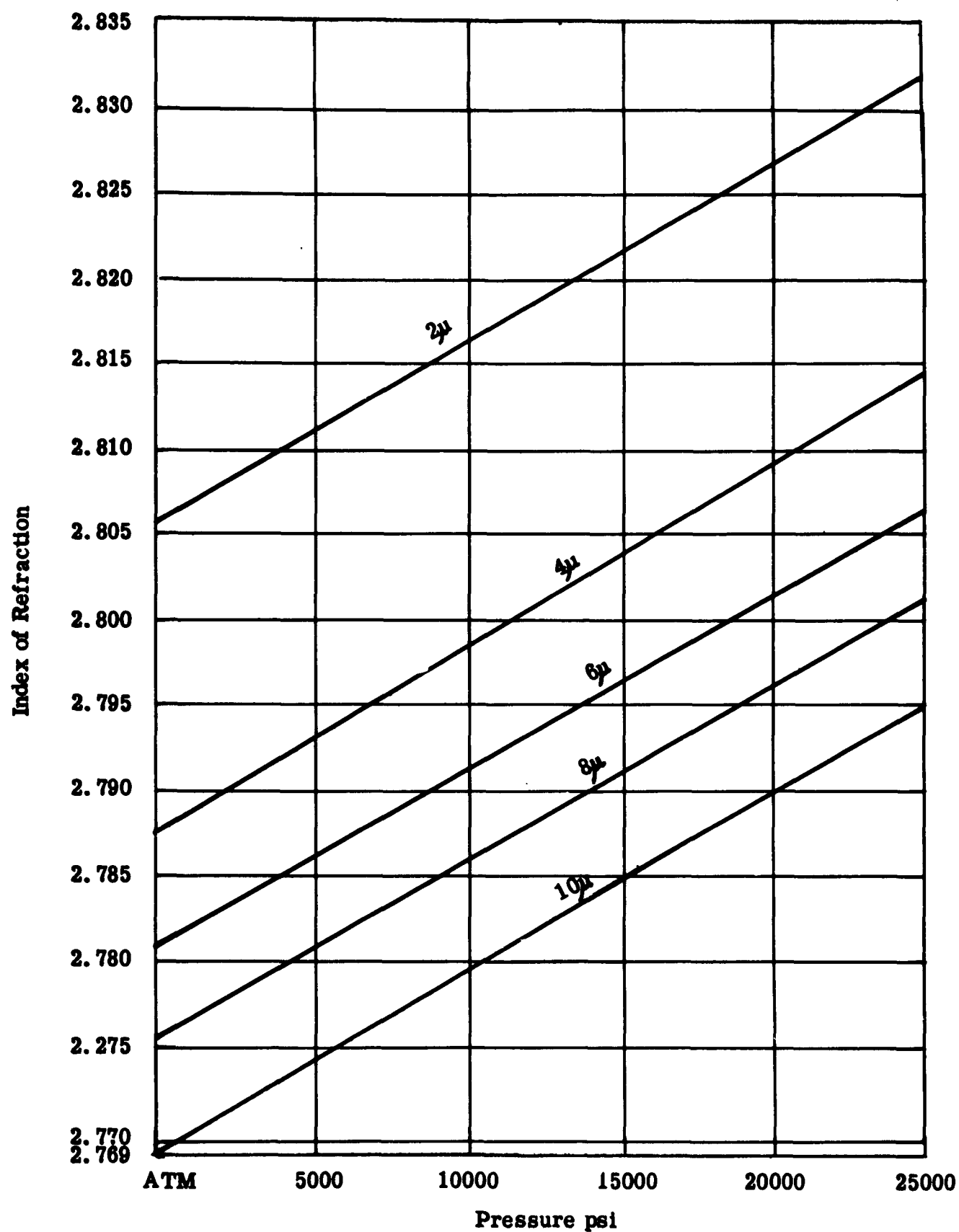
Figure 50. Variations of Refractive Index with Pressure $As_2 Se_3$ Glass
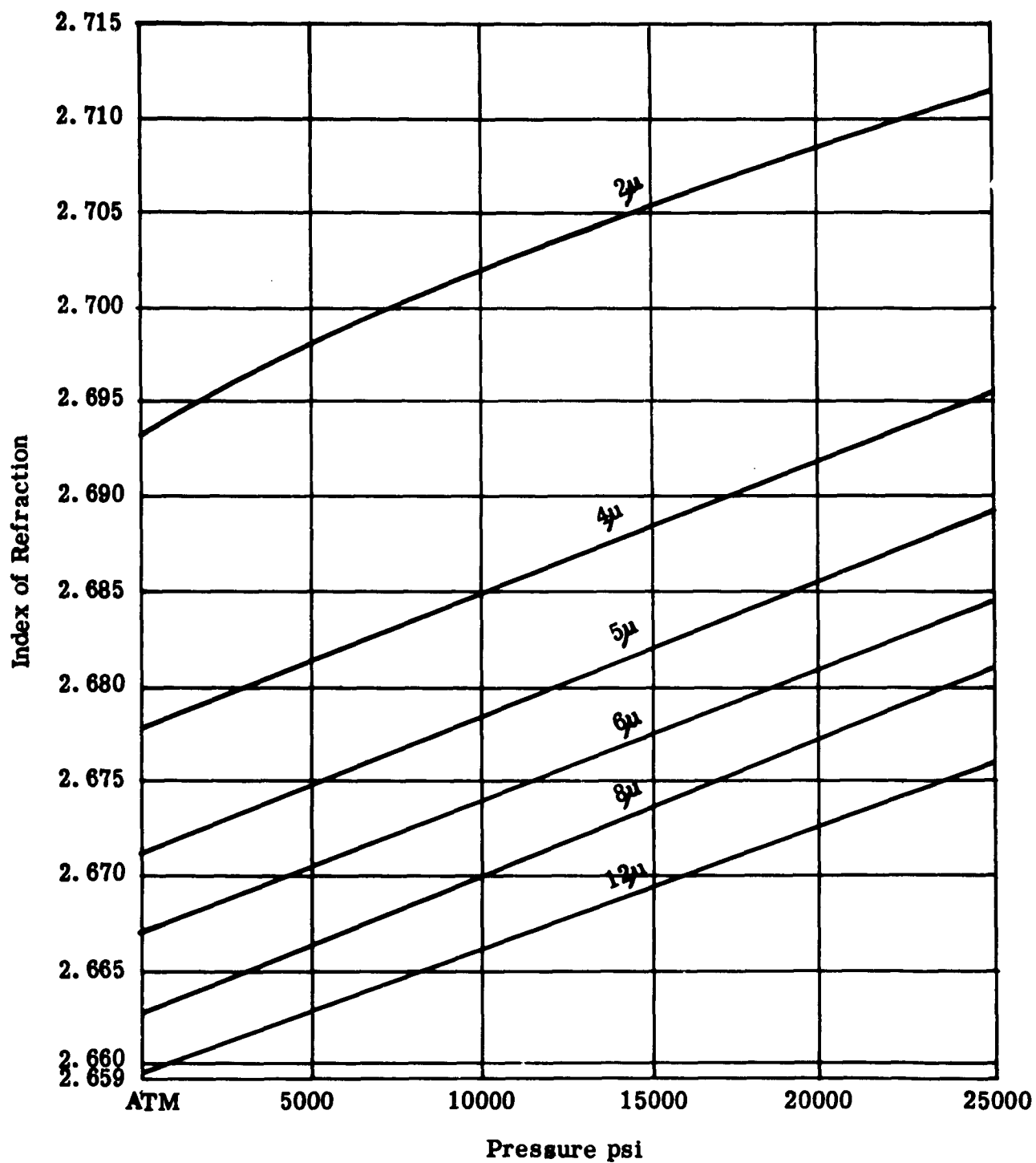
Figure 51. Variations of Refractive Index with Pressure $As_2 Se_5$ Glass

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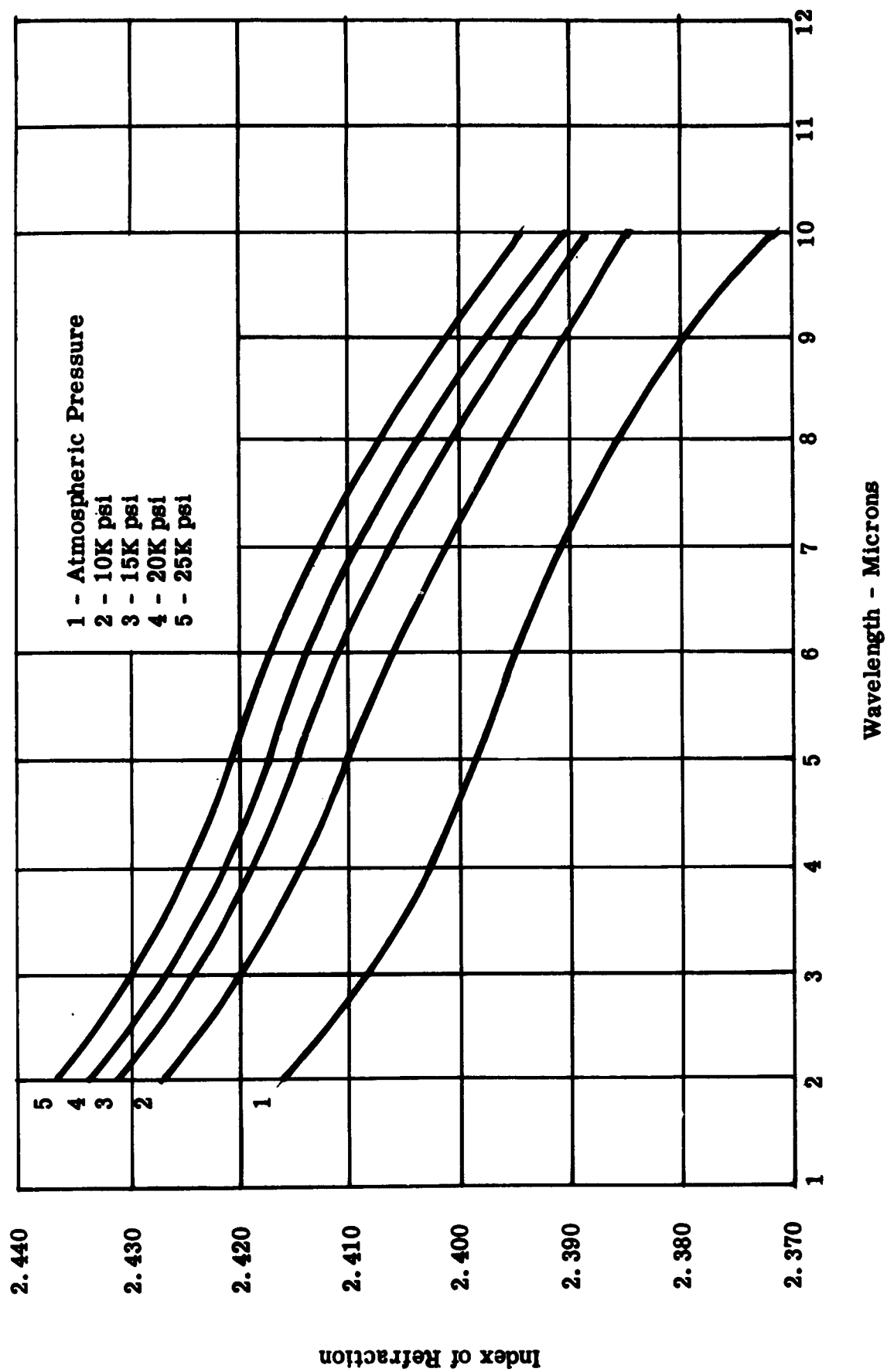
Figure 52. Variation of Dispersion with Pressure $As_2 S_3$ Glass
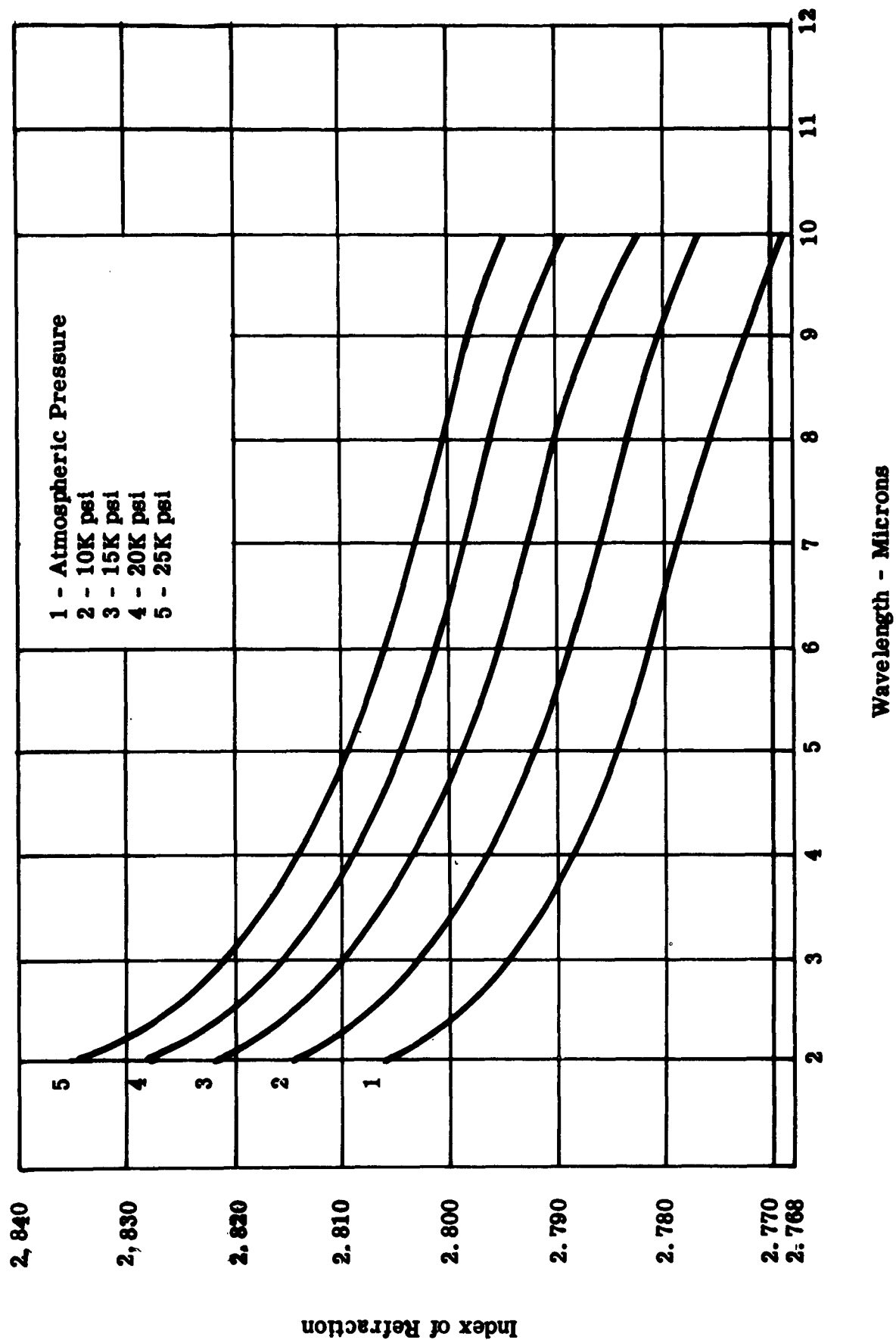
Figure 53. Variation of Dispersion with Pressure $As_2 Se_3$ Glass

1 - Atmospheric Pressure
2 - 10K psi
3 - 15K psi
4 - 20K psi
5 - 25K psi

Wavelength - Microns

Index of Refraction
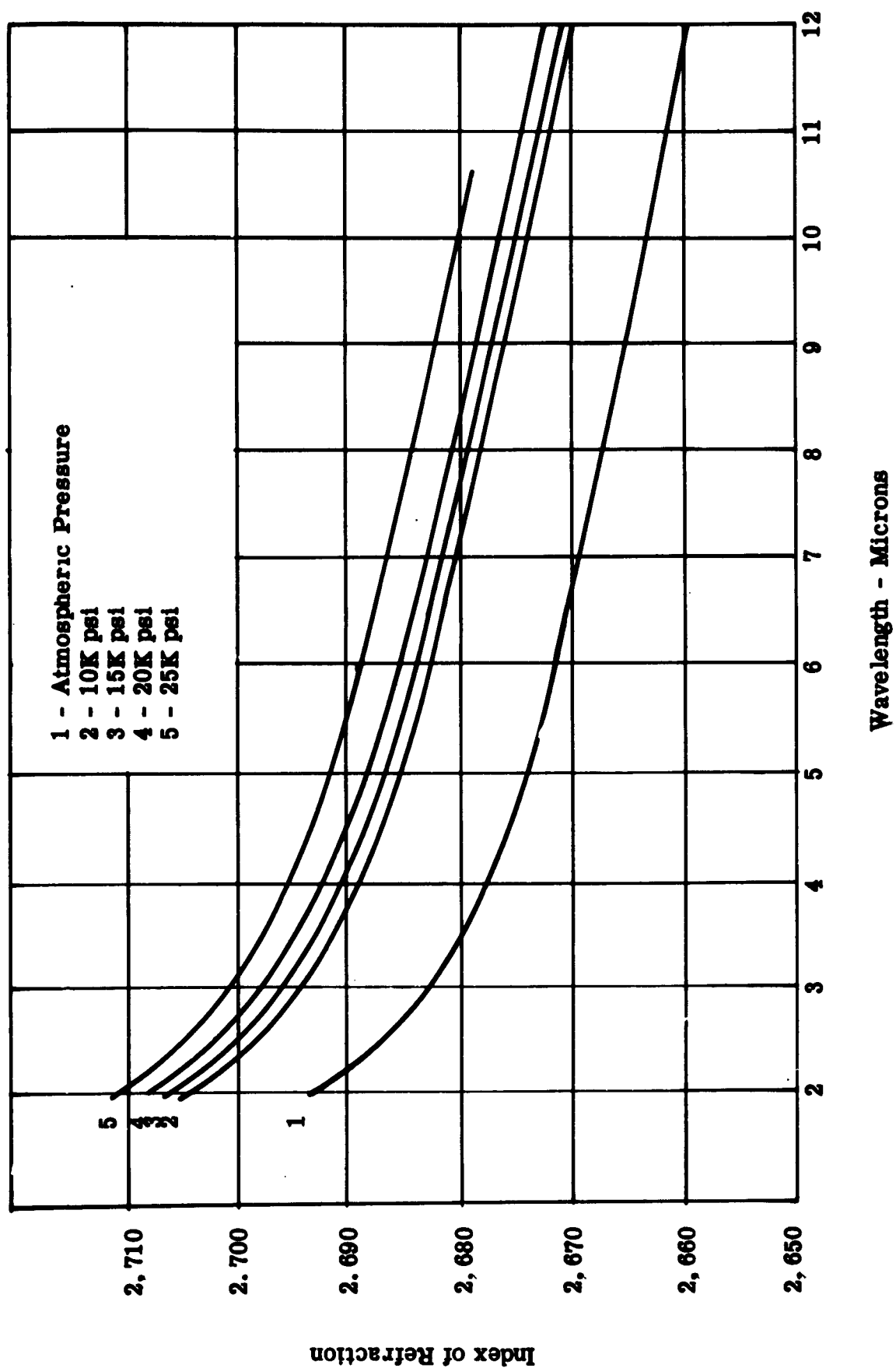
Figure 54. Variation of Dispersion with Pressure $As_2 Se_5$ Glass

8.2 The overall density change after compression was least in As_2S_3 and greatest in As_2Se_3. The compaction of As_2Se_3 and As_2Se_5 was about equal. The residual change in density after reheating, however, was much less in As_2Se_5 than in either of the other two materials.

As As_2Se_5 differed also in the rate of change of density with pressure. It is apparently beginning to approach a limiting density value as indicated by Figure 48. As_2Se_3 and As_2S_3 on the other hand, show density changes that are directly porportional to pressure and apparently could be compacted to a substantially greater extent with increased pressure. The limiting density, which would be that of the crystalline modification of the compound, would be less than of As_2Se_3 because of the smaller number of cross-linking arsenic atoms in the structure.

8.3 The refractive index variations are in line with what would be expected from the change in densities. Unfortunately, insufficient time was available to perform an index of refraction study on the As-Se-Ge glasses, since these measurements are considerably more sensitive and precise than the density data.

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8.4   A comparison of the relative compactions of the arsenic sulfide and
selenide compounds and the As-Se-Ge glasses leads to the conclusion
that the generally accepted two dimensional model of the structure
of the arsenic sulfide and selenide glasses is in accordance with their
behavior under pressure. That is, that these materials have three-
fold coordination and consist of chains or laminae of Se-Se atoms
which are cross-linked by arsenic. This structure would lead to a
low degree of compaction which would be to a great extent elastic
as evidenced by the small amount of residual density increase after
reheating.

The introduction of germanium, on the other hand, would be expected
to produce a three dimensional structure having fourfold coordination.
This type of structure would have characteristics equivalent to those
of silicate glasses in the respect that there would be an irreversible
change in density under high temperature - pressure conditions due to
a collapse of the cellular structural units. The results of these pres-
sure experiments bear out this concept of the structure of these glasses.

The three dimensional bonding is also indicated by the generally higher
softening and melting temperatures of the germanium glasses. A con-
siderably smaller amount of energy is required to break the weak
arsenic-selenium cross-linkage than is required to rupture the ger-
manium bonding.

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9. Investigation of Elevated Temperature-Pressure Effects: Recommendations

9.1 In order to obtain a more complete structural understanding of the chalcogenide glasses, further temperature-pressure studies are recommended.

9.2 The effects of time on compaction should be studied and the limiting densities determined.

9.3 Additional density studies at higher temperatures and refractive index determinations are needed on germanium containing glasses.

9.4 If possible, density or refractive index, or both, should be measured while the materials are under pressure in order to derive quantitative information regarding structure.

APPENDIX I

EXPERIMENTAL PROCEDURES AND EQUIPMENT

1. **Preliminary Glass Melts**

    Raw materials for initial evaluation melts were weighed to the nearest
    0.1 gram and combined to produce 50 grams of glass. Purity of the
    raw materials was 99.99+%. The ingredients were contained in an
    evacuated, sealed Pyrex glass tube about 22 mm I.D. x 30 cm long which
    was enclosed in a Pyrex glass protection tube. This combination was
    placed in a vertical resistance furnace with the open end of the protection
    tube projecting out of the top of the furnace.

    The furnace temperature was controlled with an on-off pyrometer con-
    troller, power being supplied through a Variac. Glasses were melted
    at temperatures from 500 to 550°C depending on their composition and
    ease of melting.

    Stirring was accomplished by removing the tube and tilting end for end
    periodically until no evidence of unmelted batch remained. The melt was
    then cooled in place at the normal cooling rate of the furnace (power off).

    After reaching room temperature, the samples were removed from the
    Pyrex tubes and examined for evidence of crystallization, bubbles, in-
    complete melting, etc. The freshly broken surface of a cleaved segment
    was examined microscopically for final quality grading.

I-1

2. Pyramid Softening Temperature

Three pyramids of glass, approximately 1/4 inch square at the base and 1/4 inch high, were placed on a flat glass plate in equilateral configuration in an oven at $70^{\circ}C$. A circular disc of glass weighing 16.5 grams was mounted on top of the pyramids so that its weight was distributed equally on all three. After stabilization, the temperature was maintained constant for 15 minutes and the glasses were examined for evidence of deformation of the pyramid points. If no deformation was observed, the temperature was raised in $5^{\circ}C$ increments and held for 15 minutes at each temperature until the "pyramid softening temperature" was reached.

3. Glass Melts for Property Determination

Specimens for property determinations were melted in 200 gram batches encapsulated in Pyrex glass envelopes under vacuum. The thermal cycle was determined from preliminary thermal properties obtained for each composition. It was necessary to know the approximate annealing characteristics in order to cool the glasses at such a rate as to avoid thermal stresses in the finished glass. All of the melts were held at approximately $550^{\circ}C$ until batch-free.

Stirring was done periodically by removing the tube from the furnace and tilting back and forth until thorough mixing was accomplished. After ascertaining that melting was complete, the melts were cooled slowly to a temperature below the critical point and the furnace power was turned off. From these melts, samples were prepared for property measurements.

4. Optical Properties

    4.1 Infrared Transmittance

        Infrared transmittance from 2 to 16 microns was measured on a
        Baird Recording Spectrophotometer. Specimens were cut, ground
        and polished to 2 mm thickness and approximately 20 mm diameter.
        In all measurements, the 100% and zero traces of the instrument
        were recorded. The transmittance curves were normalized for 0% and
        100% line variations.

    4.2 Infrared Reflectance

        Infrared reflectance from 2 to 16 microns was measured on the Baird
        Spectrophotometer. Specimens were approximately 2 mm thick by
        20 mm diameter. One side of each sample was polished and the other
        side was ground. Reflectance was measured on the polished surface
        at an angle of about 15° from normal. The back side of the specimen
        was ground with a convex radius of about 9" to prevent back reflectance
        of transmitted radiation.

    4.3 Refractive Index

        4.3.1 Infrared Rapid Refractometer

            See Figure I-1. The .008" aperture is illuminated by a quartz
            lamp. A narrow band-pass filter and a chopper are inserted
            between the source and the aperture. The relay lens which is
            a doublet pair, back-to-back, f/1.5, 2.2 inch f.1., diffraction
            limited in resolution, images the aperture at a point in space

I -3
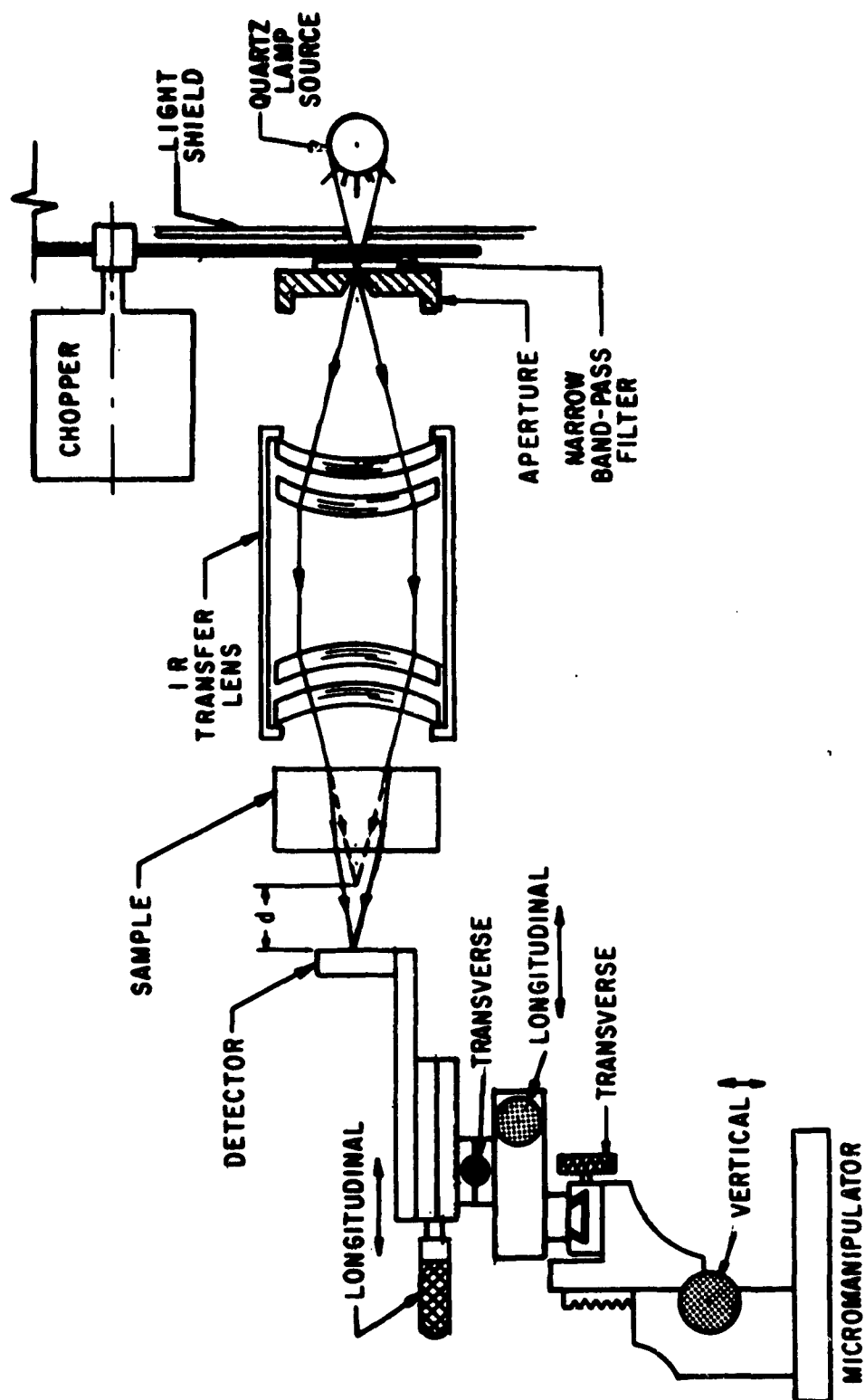
INFRARED RAPID REFRACTOMETER

Figure I-1

where it is picked up by a detector mounted on a micro-manipulator. The glass to be measured is fabricated as an optically polished, plane-parallel specimen and inserted between the lens and the detector. The detector is then adjusted to relocate the image and the distance, d, measured with the longitudinal micrometer.

4.3.2   In order to measure accurately the refractive index of materials in the infrared region, it is necessary to choose a technique in which the variation in index produces a significant, physically measureable change. To accomplish this, a monochromatic, parallel beam is refracted through a prism made of the specimen material, and the angle at which the energy emerges from the prism is a function of its refractive index at this particular wavelength.

In practice there are two approaches to this procedure. One approach determines the angle of minimum deviation of the sample prism and is fully refractive, while the second employs a reflection based on a Littrow mirror. The refractometer constructed at Servo Corporation was based on the latter approach. The arrangement of the optical system is shown in Figure I-2.

Parabolic
Collecting Mirror
M5

Detector

Detector Bias, Amplifier,
Voltmeter

Collimator:
18º Off-Axis
Paraboloid Reflector
M3

Sample Prism

Folding Mirror M-4

Auto Collimator

Precision Rotary Table

Source Folding Mirror M2

Globar Source

Parabolic
Collecting Mirror
M5

Detector

ollimator:
8º Off-Axis
iboloid Reflector
M3

Perkin-Elmer
Model 99 Monochromator

Globar
Power
Supply

S2

S1

Source Focussing Mirror
MI

Water Inlet

olding Mirror M-4

Water Outlet

Folding Mirror M2

Figure I-2 - Infrared Refractometer

Globar Source

2

The radiation from a globar is focused on the entrance slit

(S1) of a monochromator. The monochromator produces

essentially monochromatic radiation focussed at the exit

slit (S2). The off-axis parabola (M3) collimates the beam

which is reflected so that it is incident on the prism sample

being measured. The angle of the prism is calculated to

eliminate total internal reflection. The back surface of the

prism is coated with vacuum deposited gold to increase its

reflectance. This surface produces the Littrow effect.

The prism is oriented by rotation of the precision table so

that the deviated beam is collected by the parabola (M5)

and focussed on the detector. The signal is amplified and

fed into a vacuum tube voltmeter. The peak is determined

by locating the position which produces the maximum reading

on the voltmeter.

The initial position of the prism is determined by the auto-

collimator. This establishes the orthogonality of the reflec-

tive prism face and the axis of the collecting mirror, since

the autocollimator is aligned with the collecting mirror and

detector. Thus, the rotation of the prism from autocollimator

is measured. In this setup, the deviation angle is measured

for each prism. The instrument angle is a function of the initial

alignment of the system, and is a constant. The angle of the

prism is also measured by autocollimation and from this data, the refractive index is calculated. With reference to Figure I-3, the formula for calculating the refractive index is derived as follows:

If α = angle of prism,

ϵ = angle of rotation,

$\beta = \alpha + \epsilon$

μ = deviation angle

I_n = angle of ray with normal before refraction or reflection

I_n' angle of ray with normal after refraction or reflection

$I_2' = -I_2$

$\sin I_n' = \dfrac{1}{N} \sin I_n$ (Snell's Law)

From the diagram it can be seen that:

$I_3' = \epsilon + \alpha = \beta$

$I_1 = I_3' + \mu$

then $I_1 = \beta + \mu$

Following the ray through the prism and applying the above formulae produces

$$\sin \beta = N \left[\sin (2\alpha - I_1') \right]$$

where
$$\sin I_1' = \frac{\sin (\beta + \mu)}{N}$$

FIGURE I-3

GEOMETRIC REPRESENTATION OF DEVIATION METHOD

α = Prism angle

ε = Angle of rotation

β = $\alpha + \varepsilon$

μ = Deviation angle

Auto-collimator Axis

To Collector

From Collimator

Reflective (Littrow) Surface for Peak Reading

Reflective (Littrow) Surface at Autocollimating Position

$$\cos I'_1 = \frac{1}{N} \times \sqrt{N^2 - \sin^2 (\beta + \mu)}$$

expanding the sin equation and substituting, then

$$\sin\beta = \sin 2\alpha \sqrt{N^2 - \sin^2 (\beta + \mu)} - \cos 2\alpha \sin (\beta + \mu)$$

Solving for N:

$$N = \sqrt{\frac{\sin^2\beta + 2 \cos 2\alpha \sin (\beta + \mu) \sin\beta + \sin^2 (\beta + \mu)}{\sin^2 2\alpha}}$$

From the geometric location of the components in the instrument (see Figure I-2) it is known that $\mu = 28.075^{\circ}$

Therefore

$$\sin\mu = 0.470620$$

$$\cos\mu = 0.882332$$

This value of μ was verified using germanium and CaF_2 samples.

The equation now becomes

$$N = \sqrt{\begin{array}{l} (1.778510 + 1.764664 \cos 2\alpha) \sin^2\beta \\ + (.941240 \cos 2\alpha + .830486) \sin\beta \cos\beta \\ + .221483 \cos^2\beta \end{array} \Bigg/ \sin^2 2\alpha}$$

Once the prism angle is known, the formula simplifies even further.

A typical calculation is as follows:

Prism 62-76-B-3 has angle of 14° 59' 23" $= \alpha$

$\sin 2\alpha = .4990689$

$\sin^2 2\alpha = .249689$

$\cos 2\alpha = .866205$

$$N = \sqrt{\frac{3.07071 \sin^2 \beta + 1.645793 \sin\beta\cos\beta + .221483 \cos^2 \beta}{.249689}}$$

At 2μ, $\epsilon = 21^O$ 45' 30"

Therefore $\beta = 36^O$ 44" 53"

$\sin \beta = .59811$

$\cos \beta = .80141$

$\sin^2 \beta = .35774$

$\sin \beta \cos \beta = .47933$

$\cos^2 \beta = .64226$

$N^2 = 8.46733$

$N = 2.910$

ϵ varies for each wavelength and the variation in N can be seen in the charts shown in the text.

A program was setup for IBM 7094 computer to calculate automatically refractive index from the above data.

4. Thermal Properties

4.1 Thermal Expansion, Critical and Softening Points

These properties were measured on a Gaertner Dilatation Interferometer. The Gaertner Interferometer utilizes the principle of interference of light to measure thermal expansion.

Three samples of the specimen material are prepared in the shape of pyramids and placed on an optical flat. The height of the pyramids is approximately 1/4 inch and all must have equal height within 0.0001 inch in order to produce the proper interference fringe pattern. The specimens are positioned equilaterally and a second optical flat is placed on top of the pyramids. A parallel beam of light is projected from a mercury source (5460A wavelength) onto this assembly, and the heights of the pyramids are adjusted by grinding the bases until a suitable fringe pattern is obtained between the plates. The fringes are contour lines of the space between the plates. When the plate separation changes due to the expansion of the specimens, the fringes move one fringe width for an expansion equivalent to a 1/2 wavelength of green light (2730A).

To measure expansion, the interferometer plates and specimens are contained in a furnace which is heated at a linear rate. During this heating, the fringes passing a reticle in the eyepiece of the telescope are counted and the temperature recorded for each fringe. The number of fringes multiplied by .000273 gives directly the expansion of the

material in millimeters. A plot of temperature vs. change in
length provides a graphical method of calculating expansion over
various temperature ranges. This plot also gives the critical
and softening points of the glass.

4.2   Thermal Conductivity

The Cenco-Fitch Thermal Conductivity Apparatus, Cenco No. 77555,
was used to measure thermal conductivity. This apparatus is specially
designed for the measurement of poorly conducting materials such as
paper, fabrics, wood, cork and glass.

A thin piece (less than one centimeter thick) of the material to be
measured is placed between an upper vessel kept at constant tempera-
ture and a lower insulated block of copper of known thermal capacity.
The temperature increase of the copper block due to heat conducted
through the specimen material is measured. Thermocouples and a
potentiometer are used to indicate temperatures. From the rate at
which heat is conducted through the material, and the area, thickness,
and temperature differences of the faces of the specimen of material,
its thermal conductivity is calculated.

Specimen size for the 20 glasses in this report was 52 mm diameter by
2.5 mm thick. All samples were polished on both faces and coated with
a thin layer of silicone grease to assure intimate contact between the

heat source and sink. The sample was attached to the heat source with silicone grease and the water inside brought to a boil. After boiling for 5 minutes the heat source and sample were placed on top of the heat sink. Differential temperature readings were taken every 30 seconds until a total of ten readings were accumulated. From these data the thermal conductivity was calculated.

4.3 Reworkability

Reworkability is an important property in handling these materials since many different sizes and shapes are needed for lens components. This attribute was determined by molding the specimens used for thermal conductivity measurements. A solid cylinder of glass was placed inside a mold made from Pyrex glass tubing. This arrangement was placed inside an oven and the temperature raised to $300^{\circ}C$. After holding for 30 minutes the glass flowed enough to assume the shape of the mold which was then transferred to another oven held at the annealing point of the glass. After annealing for 15 minutes the temperature was lowered slowly to room temperature.

4.4 Specific Heat

Specific heat was measured on a Cenco No. 78044 Vacuum Jacketed Calorimeter. This apparatus consists of a jacketed container with cover into which is fitted a calorimeter cup. The jacket container is comprised of a large Dewar flask with silvered surfaces, enclosed in

a cylindrical metal case. The case supports a cover with openings for a stirrer and thermometer and a central opening for the introduction of material into the calorimeter well.

Specimens were heated to 100°C in boiling distilled water and kept at this temperature for 30 minutes to assure equilibrium. The sample was then dropped into water at room temperature in the calorimeter well.

Temperature readings were taken every 30 seconds after introduction of the sample until the temperature reached a maximum.

From these data, the heat lost by the glass specimen is equated to the heat absorbed by the water and calorimeter, and the equation is solved for specific heat of the speciment.

5. Chemical Durability

This test consists of placing a sample having a known weight and surface area of glass into a solvent of known concentration in a test tube which is immersed in a water bath at constant temperature for 6 hours. The sample is then reweighed and the weight loss per unit surface area of the specimen is then calculated. The following conditions were maintained during the test:

Sample size	.29" x .29" x .29" (approx.)
Surface area	.5 sq. inch (approx.)
Sample weight	0.8 to 1.8 grams
Reagent volume	10 ml
Time of soaking	6 hours

Reagent	Concentration	Water Bath Temp.
NH_4OH	0.4 Normal	$60^{o}C$
KOH	0.3 Normal	$60^{o}C$
HCl	1.0 Normal	$60^{o}C$
HNO_3	1.1 Normal	$60^{o}C$
H_2SO_4	2.1 Normal	$60^{o}C$
Ethyl alcohol	90% by Volume	$60^{o}C$

6. Electrical Properties

Specimens for dielectric constant were 2" diameter x 0.1 thick. They were mounted in a General Radio Type 1690A dielectric sample holder and were subjected to a test frequency of one megacycle. Measurements were made by means of a General Radio Type 716C capacitance bridge at room temperature. The test was made at New York Testing Laboratories, 81 Urban Avenue, Westbury, L. I., N. Y.

Specimens for resistivity determination were 20 mm dia. x 2.0 mm thick, polished on both faces. The sample was clamped between two electrodes and a saturated sodium chloride solution was used to assure intimate contact between sample and electrodes. The electrode leads were connected to a megohmmeter.

Readings of resistance were taken at 500 volts and the resistivity calculated from the relationship:

where $\quad\rho$ = Resistivity in ohm cm

$\qquad\qquad$ R = Resistance in ohms

$\qquad\qquad$ A = Area of one surface

$\rho = \dfrac{RA}{\ell}$ $\qquad\ell$ = Sample Thickness

7. **Physical Properties**

Knoop hardness was measured at New York Testing Laboratories using a Leitz Durimet instrument fitted with a Knoop diamond point indenter under 100 gm load.

Young's Modulus and tensile strength were measured on a Cenco No. 73920, Flexure of Beams Apparatus. Young's modulus was determined by loading a uniform rectangular bar midway between the supports in three point loading. The deflection of the beam was measured with a micrometer screw equipped with an electrical contact. From the load applied, the deflection and the physical constants of the apparatus and specimen, the modulus was calculated. An average of three samples was taken for each glass.

Tensile strength was also measured on the flexure equipment by loading a rectangular bar in three point configuration. The load was gradually increased by filling with water a container suspended from the sample. The load at the instant of sample failure was weighed to ascertain the breaking load which

established the breaking strength.   An average of three samples were taken.

Compressive strength samples were 1" diameter and 1-1/2" high. Specimens were tested in a calibrated Tini us Olsen Universal Testing Machine at New York Testing Laboratories. The upper and lower heads were of the ball and socket type. Samples were set between the heads and adjustment was made in the ball sockets so that the load was applied with the specimen in a vertical position. Paper shims were placed between specimens and loading plates to compensate for any surface irregularities. Because of the manner of loading, specimens started chipping between 1000 and 1500 lbs. Low strength specimens started chipping at a few hundred pounds.

APPENDIX II

STUDY OF VALIDITY OF MEASURED DATA

According to Borg[+], the equation:

$$C = \frac{\alpha E}{2\rho(1-2r)} \tag{1}$$

which can be rewritten as,

$$\rho = \frac{\alpha E}{2C(1-2r)} \tag{2}$$

where C = specific heat

α = coefficient of thermal expansion

E = Young's modulus

ρ = density

r = Poisson's ratio

can be used to evaluate the accuracy of measurements made on materials
which are homogenous and whose elastic properties follow Hooke's law.
It is evident from the Stress-Strain curves that these glasses obey Hooke's
law quite well, therefore the above equations should be applicable to
property data obtained in this investigation.

[+]Borg S. F., Machine Design 36, 18, 113 (1964)

II-1

Although Poisson's ratio was not determined for these glasses, a value
can be approximated from the measured values of the other variables.

Using mean values of the properties α, E, C and ρ for the glasses
investigated in equation (2) and solving for Poisson's ratio (r)

$$\rho = \frac{\alpha E}{2 C (1 - 2 r)}$$

$\alpha = 31 \times 10^{-6}/C^{o}$

$E = 1.75 \times 10^{6}$ psi
  $= 1.23 \times 10^{8}$ gm/sq. cm

$C = .096$ cal/gm C^{o}
  $= 4097.9$ cm/^{o}C
  $= 3.68$ gm/cm^{3}

$$3.68 = \frac{(31 \times 10^{-6}) (1.23 \times 10^{8})}{8195.8 (1 - 2 r)}$$

$$3.68 = \frac{.468}{1 - 2 r}$$

$$r = \frac{3.21}{7.36} = .436 \qquad \text{(approximate mean value of Poisson's ratio)}$$

This approximation of Poisson's ratio satisfies the condition of equation
(2) that $r < .5$.

Substituting this mean value of r into equation (2) and using the values of
α, E and C measured for representative glasses gives:

Glass No. A-161

$$\rho = \frac{\alpha E}{2C(1-2r)}$$

$$= \frac{3.9\,\alpha E}{C}$$

$$= \frac{3.9 \times 27.6 \times 10^{-6} \times 1.86 \times 10^6 \times 454}{.103 \times 42686 \times 6.54}$$

$$= \frac{3.9 \times 27.6 \times 1.86 \times .454}{.103 \times 42.7 \times 6.45}$$

$$= \frac{91}{28.4} = 3.2 \frac{gm}{cm^3} \quad \text{(calculated density)}$$

$\alpha = 27.6 \times 10^{-6}/C^o$

$E = 1.86 \times 10^6$ psi

$C = .103$ cal/gmC^o

Comparing the calculated with the measured value of density, the difference is —

$$\frac{3.35 - 3.2}{3.35} \times 100 = \frac{15}{3.35} = 4.5\%$$

Glass No. A-145

$\alpha = 21.9 \times 10^{-6}/C^o$

$E = 2.41 \times 10^6$ psi

$C = .081$

gives, $\rho = 4.11$ gm/cm^3

II-3

Comparison with measured value of density gives,

$$4.43 \; \simeq \; 4.11 \quad \text{or} \quad 7.2\% \text{ difference}$$

<u>Glass No. A-166:</u>

$$\alpha = 32 \times 10^{-6}/C$$

$$E = 1.67 \times 10^{6} \text{ psi}$$

$$C = .110 \text{ cal/gm } C^{o}$$

gives, $\rho = 3.07$

$$3.18 \; \simeq \; 3.07 \quad \text{or} \quad 3.46\% \text{ difference}$$

<u>Glass No. 63-127:</u>

$$\alpha = 28.8 \times 10^{-6}/C^{o}$$

$$E = 2.0 \times 10^{6} \text{ psi}$$

$$C = .119 \text{ cal/gm } C^{o}$$

gives $\rho = 3.11$

$$3.38 \; \simeq \; 3.11 \quad \text{or} \quad 8.0\% \text{ difference}$$

<u>Glass No. A-174:</u>

$$\alpha = 32.6 \times 10^{-6}/C^{o}$$

$$E = 1.68 \times 10^{6} \text{ psi}$$

$$C = .099$$

gives $\rho = 3.49$

$$3.38 \; \simeq \; 3.49 \quad \text{or} \quad 3.25\% \text{ difference}$$

Assuming that Borg's relationships are correct, this evaluation indicates a maximum deviation from theoretical of 8.0%. Considering normal experimental error and the approximation which was made for Poisson's ratio, this is considered excellent agreement. Future measurements on materials of this kind should include a determination of Poisson's ratio.